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XXXVI. *On an Electromotive Force between Two Metals in Relative Motion.*

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INTRODUCTION.

Lafay's Work.

THE phenomenon which forms the subject of this paper seems to have been first brought to light by M. Lafay, a paper † by whom on the subject appeared in 1928. It was brought to our notice by its précis published in 'Science Abstracts'‡. Lafay found that when two metals were rubbed together the seat of rubbing became a source of an e.m.f. which, according to him, was due partly to the rise of temperature (the thermo-e.m.f.) caused by friction and partly to the contact of metals. The two effects were usually in opposition, and the one due to heat could be easily eliminated or allowed for. One of the metals, the harder of the two, was given by Lafay the form

* Communicated by the Authors.

† *Comptes Rendus* of the Paris Academy of Sciences, clxxxvi. pp. 133-4.

‡ Abstract no. 1386 of 1928.

of a disk rotating at a known speed, and the other metal was pressed against the rim of the disk. He established two laws for the e.m.f. produced under the circumstances, after allowing for the thermo-e.m.f., namely :

(1) that it is proportional to the relative speed of the two rubbing surfaces, and

(2) that it is independent of the pressure with which the two surfaces are pressed against each other.

Lafay gives results only for silver and copper rubbing against steel. The greatest e.m.f. that he obtained was 8 millivolts between silver and polished steel. One of the essential conditions for getting these e.m.f.'s is the polishing of the rim of the rotating disk, but Lafay only lightly touches on the methods of polishing, and his paper gives no details of the working part of the arrangement.

A Brief Outline of our Results.

By improving the polish on the surfaces concerned we have been able to obtain e.m.f.'s considerably higher than those obtained by Lafay. The two generalizations given by him are found to be true only so long as the e.m.f.'s dealt with are of the same small order of magnitude as those that prevailed in Lafay's work. Thus, as regards the first law, with good polish, which enables one to get a fairly high e.m.f., a sort of saturation or constant value for the e.m.f. is obtained at high speeds. With respect to the second law, about the e.m.f. being independent of the pressure with which the two surfaces are pressed, this is true for only a moderate range of pressure. Lafay states that the e.m.f. observed remained unaltered for a variation of pressure between 10 and 200 grammes per sq. mm. This statement might lead one to expect that the e.m.f. generated would be independent of pressure altogether, which, however, is not the case. At very small pressures, when the " contact " is not very good, the e.m.f. is, of course, small. But at high pressures also the e.m.f. again falls to small values, even to zero. Lafay worked with only two metals against steel. We have extended the investigation to a fairly large number of metals. It is therefore considered worth while giving a few details of the arrangement used for the detection of these e.m.f.'s and the means employed for enhancing the effect.

Description of the apparatus and Methods of Observation.

It was pointed out by Lafay that the metal whose disk is to be rotated should be harder and more resisting than the one which is to be pressed against it; for if the disk be of the softer metal its surface when rubbed with the harder metal will very soon lose its polish. Moreover, the harder, stationary metal will soon get covered with particles of the softer metal of the rotating disk. Due to both these reasons the phenomenon will become masked. In our experiments, therefore, we followed Lafay in having the rotating disk always a steel one.

Mounting of the Steel Disk.

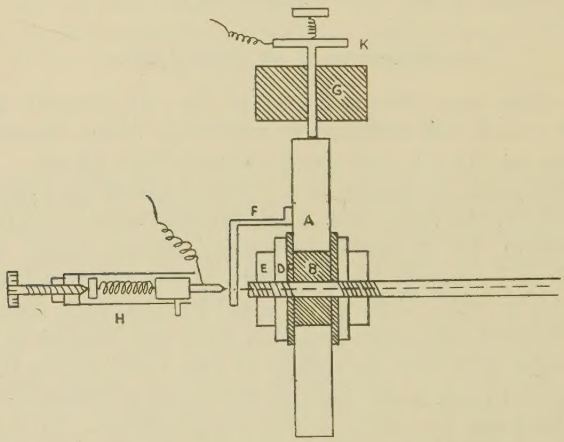
The disk was obtained out of an old disused circular saw of which the teeth were removed. The diameter of the disk was 14 cm. and its thickness about $1\frac{1}{2}$ cm. It was mounted so as to rotate in a vertical plane by supporting the disk on the same axle as a circular wheel which could be rotated by a one-horse-power motor fixed on the ground and coupled to the wheel in the usual manner by means of a belt. The wheel and the disk were fixed on a stout wooden slab attached to a wall, the slab being made quite rigid and firm by means of two iron elbows fixed to the wall supporting the slab as well as by a vertical wooden pillar between the ground and the platform. It does not seem necessary to give all the details about the mounting of the wheel. All that is sufficient and necessary is to mention that special care must be taken to ensure that the disk rotates smoothly without any jerks or vibrations.

Insulation of the Disk.

The steel disk must also be electrically insulated from the axle. This is secured by means of an ebonite disk of the same thickness as the steel disk (see B, fig. 1) fitting into the central portion of the latter and through the centre of which (the ebonite disk) passes the axle. Circular ebonite rings (C, fig. 1), used as washers against the two faces of the disk, insulate it from the binding nuts and iron washers (D and E, fig. 1). The whole arrangement is shown diagrammatically in fig. 1, in which A represents the steel disk. This insulation protects the disk from

any heat developed in other parts of the mounting as well as from any electrical disturbances arising from the motion of the wheel. These latter may be great enough at times to make sparks jump across the insulation, and seem to be due to the friction of the lubricating oil. In order to protect the disk from such great static charges the iron wheel and the frame supporting it must be earth connected; and in order to avoid any inductive effects due to the metal disk rotating in the earth's magnetic field the plane of rotation should be made to lie in the magnetic meridian.

Fig. 1.



The Speed of the Disk.

The speed of rotation of the disk can be altered by allowing the current for driving the motor to pass through variable resistances. It was measured ultimately by means of Siemen's tachometer, *i. e.*, a revolution counter, reading from 500 to 2500 revolutions per minute. Since the diameter of the disk was 14 cm., a speed of 100 revolutions per minute means a relative speed between the two metals of $\pi \times 14 \times 100/60 = 73{\cdot}3$ cm./sec. $= 0{\cdot}733$ metre per second.

The Second Metal.

For studying the variation of the e.m.f. with pressure, the second metal, the contact between which and the steel disk is to produce the e.m.f., was given the form of a rod

about 2 mm. in diameter and 4 cm. long. This was soldered to a thin circular disk (diameter about 4 cm.) of the same metal, to which was soldered the leading-out copper wire. On the other side of this disk was attached a steel spring on which was fixed a pan for taking the loads. The rod passed through a small cylindrical cavity drilled in an ebonite piece (G, fig. 1) which was screwed on to two supports fixed to the wall, such that the cavity came vertically above the top of the steel disk, so that the end of the rod could rest vertically and normally on the rim of the disk. Fig. 1 shows these points at K.

As a matter of fact, except for the preliminary experiments performed to find how the e.m.f. generated depended on the pressure with which the second metal was applied, in which a normal contact as described above had to be used, for all later work the second metal, suitably insulated, was applied to the disk holding it in the hand. The high e.m.f.'s observed could only be obtained when the metal was thus applied. To do so the metal was taken in one of the forms mentioned below according to its nature.

Thus elements like aluminium, silver, etc. were taken in the form of thick strips which could be conveniently polished and applied at the rim without bending. Elements like magnesium and platinum, which could only be procured in the form of thin sheets or ribbons, were taken in the form of a ribbon and were held on or fixed to pieces of wood. Held thus they could be easily polished and conveniently handled. Some metals, like nickel and zinc, were taken in the form of short rods, varying in diameter from 2 to 5 mm. These rods were rounded and polished at the ends to be applied. Metals which could only be obtained as irregular pieces and which could not be hammered, being brittle, like antimony, manganese, etc., were rubbed against emery stone and rough sandpaper to round off the irregularities and sharp corners.

Metal pieces taken in any of the above forms were inserted into small lengths of rubber pressure-tubings of suitable bores. Besides serving as insulating handles this device had another advantage, namely, that in the case of metals to which the leading-out copper wire could not be soldered, the wire was simply wound round the other end and this inserted into the pressure-tubing, which ensured good contact between the metal and the wire. Moreover,

such a rubber handle ensured the contact between the metal and the revolving rim being smoother and freer from jerks than it would have been if the metal were held by or fixed to some rigid support.

The Leads.

One of the leading-out wires is soldered or attached to the second metal in the way just described. To get a second point of contact a stout L-shaped silver strip (F, fig. 1) is soldered at one end to the steel disk as near the axle as permissible, the other end, the top of L, coming just in front of the centre of the axle. In line with the centre of the axis of rotation is a point on the silver strip which is practically stationary. Against it plays a pointed silver rod of diameter about 2 mm. and having the second leading wire soldered to it. The other end of the silver rod is soldered to a brass cylinder of length about a centimetre and diameter about 5 mm., which moves freely in a brass tube. This tube is held in a clamp suitably fixed, so that the silver rod is in line with the axis of rotation of the disk. The brass cylinder is pushed forward by means of a steel spring which can be worked to and fro by means of a screw. The screw is provided with a nut, which is tightened up when the contact has been adjusted. The nut is to prevent the movement of the screw due to vibrations. When the contact with the disk is not required the solid brass cylinder is pushed back by the hand and is locked by turning it to the side. The arrangement for the second lead is shown at H in fig. 1.

Preparation and Polishing of the Steel Disk.

As already mentioned an old circular saw was used as the revolving plate in these experiments. It was first distempered, and then mounted on a lathe, its teeth removed, and the faces and the rim cleaned of all hollows and scratches. After this the plate was again tempered, remounted on the lathe, and the rim polished against a piece of broken emery wheel or grindstone, using a "special grinding compound" as lubricant. This process also makes the rim perfectly circular.

The circular plate was then fitted on the mounting in the way already described and the polishing of the rim continued with various grades of emery paper, beginning with

the coarsest and ending with the finest. The polishing is the most tedious part of the experiment, but it is also the most important, as on the extent of the polish alone depends the strength of the e.m.f. obtained. It is not mere cleanliness of the surface that is required, but mirror smoothness. To attain this the surface of the emery paper in the final stages, when the very finest paper is being employed, should be changed every minute or so of rubbing it against the rim of the disk, and the process continued till the emery surface does not get blackened at all. The finishing touches to the polish are given by *light* application of the paper for a long time, and finally polishing up with a piece of chamois leather. Polishing with French chalk was found to be not essential.

Conditions for getting the Maximum Effect.

The surface of the second metal should also be similarly treated to attain a high polish. The final test as to whether sufficient polish has been attained or not is to take readings on the measuring instrument of the e.m.f. generated when the second metal is pressed against the rim of the rotating plate. By experience one can judge whether the maximum possible e.m.f. with the metal used is being obtained or not. If not, the polishing should be continued till the maximum voltage is obtained. It should be mentioned here that the maximum effect can only be obtained when, besides the polish on the rim and the second metal being as perfect as possible, the contact between the two metals is also perfectly smooth—there is no up-and-down motion of the rim, nor is there any sound produced when the two metals are in sliding contact with each other. When jerks are present the so-called contact is, of course, not continuous, and if there is any sort of sound produced by the contact, or, rather, by actual rubbing of the second metal against the surface of the rim of the revolving steel disk, the effect is again altogether marred.

The statement just made suggests that the so-called contact we are here dealing with is not an actual metallic contact between the two metals, but only a very close juxtaposition between the two surfaces. In fact, there should be no actual rubbing of the two surfaces in order to get the desired effect. As the experiment progresses, however, a certain amount of actual rubbing must take

place which tends to spoil the polish, particles of the softer metal applied being deposited on the steel surface, so that if the experiment is continued for long the e.m.f. begins to fall. The metal particles deposited on the steel surface may be so small that they may remain invisible to the unaided eye, but they must be removed in order to get back the higher e.m.f. The removal can, of course, be brought about by repeating the processes of polishing. It need hardly be mentioned that when beginning with a new metal all traces of the one previously used on the steel surface must be thoroughly removed.

It seems to be worth while here to point out again what has already been alluded to, that to get the maximum effect the second metal must be applied on the rim of the steel disk tangentially, holding it with the hand. The maximum effect was never obtained by applying the second metal vertically and normally. In fact, with such an application of the metal (which was used only in the preliminary experiments to study the effect of pressure, with which the contact is made, on the generated e.m.f.) the voltage often fell with great rapidity to a small value, sometimes even to the neighbourhood of zero, in agreement with Lafay's observations. On the other hand, when the metals were applied with the hand tangentially the fall was not so sudden and the high values of the e.m.f. obtained could be maintained fairly constant for some time. It must be said though that there is probably nothing inherently objectionable to the normal application of the second metal. All that is necessary to obtain the greater effect is that the application of the second metal must be light, so that there is no actual rubbing of the surfaces, and the tangential application lends itself to such a light application much more readily and easily than the normal.

A motion of the second metal to and fro at right angles to the direction of motion of the rim of the steel disk not only increased the effect in most cases but served also to keep it more steady. Sometimes the maximum effect could not be obtained if the second metal were applied immediately after the steel disk was polished with emery paper to remove the foreign particles, but after waiting for some time the higher values could be obtained. This behaviour is significant and will be referred to later on.

Method of Measuring the E.m.f.'s.

The e.m.f.'s generated were measured by means of a previously calibrated galvanometer, the leads from the rotating disk and the applied metal being connected to its terminals. What is thus measured is really the current flowing through the instrument; but knowing the total resistance in the circuit, the e.m.f. generated can be calculated, and it is these calculated e.m.f.'s that are given in the sequel. The resistance of the galvanometer itself was of the order of a hundred ohms, but resistances of 20,000, 30,000, 100,000, and 200,000 ohms could be placed in series according to requirements. The contact resistance between the applied metal and the rim of the disk while rotating was of the order of 4000 ohms (determined by Mance's method of measuring resistances). The galvanometer deflexions, when any one of the four resistances mentioned above were in series, were previously calibrated in the usual manner.

We have used this method for measuring the e.m.f.'s in place of the potentiometer method employed by Lafay, for, as will be mentioned again later on, the high e.m.f.'s obtained by us could not be maintained constant for any length of time, so that the potentiometer method of balancing and getting a null point in every case would not have been suitable.

The Thermoelectric Part of the Effect.

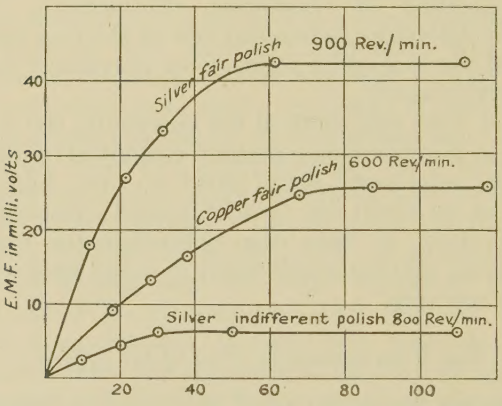
There seems to be no need to take into account the thermoelectric e.m.f.'s in the present stage of these experiments. True there must be a small e.m.f. at the metal steel junction which gives rise to thermoelectric effects, but that has no resultant effect so long as the temperature remains the same throughout the circuit. In the present experiments there would hardly be any rise of temperature at the metal steel junction, for there should be really no actual rubbing of the two surfaces in order to obtain the effect properly. Anyway the method of producing and measuring the e.m.f. called into play by the relative motion is in its present form not so exact and refined as to justify taking into consideration or allowing for comparatively such minute effects as the thermoelectric.

Results and Discussion.

Lafay's Second Law.

The preliminary experiments were performed to test the two laws given by Lafay and mentioned above. These were thoroughly studied between polished steel and silver, copper and aluminium. As remarked in the beginning, we find that his second law—that the generated e.m.f. is independent of the pressure on the surface of contact—is rigidly obeyed within certain limits of pressure. Thus there is, of course, a minimum value for the pressure to get the full effect, namely, the pressure which is necessary to

Fig. 2.



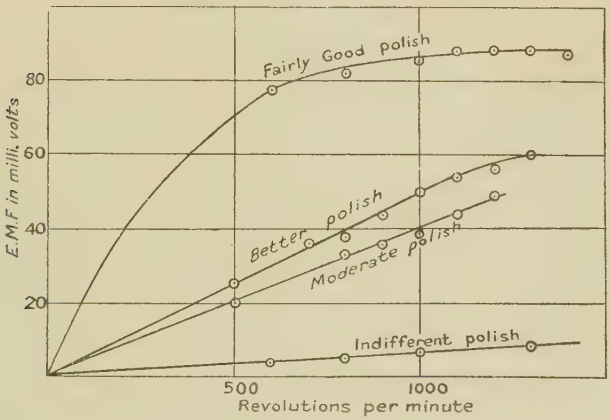
Total load on the surface of contact in grams.

maintain a uniform contact, or, rather, the so-called contact, between the two metals. Increasing the pressure beyond this does not increase the effect till the pressure is considerably increased, when it rapidly falls and disappears. In Table I. is shown how a minimum pressure is necessary to produce the full effect, and that increasing the pressure beyond this does not increase the e.m.f. generated. The curves in fig. 2 are plotted from this table. In these experiments the second metal was applied normally and mechanically, and pressures were not increased to such an extent as to get the diminution of the effect. Such diminution was noticed when the metal was applied with the hand.

Lafay's First Law.

With respect to the first law given by Lafay—that the generated e.m.f. is proportional to the relative speed between the two metals, so that the curve between the speed and the e.m.f. should be rectilinear—we find that this holds (1) for all speeds when there is only a small amount of polish on the steel rim, and (2) for only small speeds when the polishing is improved. With the high degree of polish that we imparted to the surfaces concerned we find that as the speed increases the generated e.m.f. does not keep on rising proportionately, but tends to reach a saturation value, so that with high speeds (and a high degree of

Fig. 3.



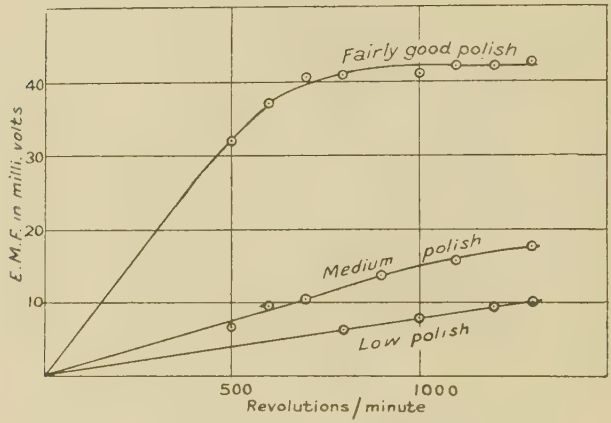
E.M.F. generated between silver and steel.

polish) the e.m.f. is independent of the speed as well. This is clearly exhibited in the curves of fig. 3 for silver and fig. 4 for copper, the details for which are given in Table II.

The Highest e.m.f.'s obtained by us.

The maximum e.m.f. obtained by Lafay as given in his paper was 8 millivolts between silver and steel. Between copper and steel he obtained 0·16 millivolt. The highest e.m.f. between silver and steel that we have been able to get so far is 123 millivolts, and between copper and steel 82 millivolts. The very highest e.m.f that we have been able to obtain is between aluminium and

Fig. 4.



E.M.F. between copper and steel.

TABLE I.

Showing the variation of e.m.f. with pressure.

Metal		Silver.	Silver.	Copper.
Remarks about polish		Indifferent.	Fair.	Fair.
Speed of the disk (rev./min.)		800	900	600
Diameter of the surface of contact (mm.)		2·82	2·30	2·51
Area of the surface of contact (sq. mm.)		6·26	4·16	4·95
Weight of the scale-pan (grams)....		10·0	11·9	18·1
E.m.f.'s (millivolts) generated with weight (grams) on the scale pan	Empty	2·5	17·4	9·1
	10	4·2	26·7	13·0
	20	6·2	33·2	16·2
	40	6·4	—	—
	50	—	42·5	24·8
	70	—	—	25·9
	100	6·4	42·5	25·9
Approximate minimum pressure (gms./sq. mm.) necessary to produce the full effect (from the curves of fig. 2)		6	13	14

steel, its magnitude being 730 millivolts and its direction opposite to that between silver or copper and steel. It may be noticed that the maximum values of e.m.f.'s for copper and silver given in this paragraph and given later in Table III. are considerably higher than those given in Tables I. and II. and shown in the curves of figs. 2, 3, and 4. These higher values are the results of later experiments.

Extension to other Metals.

It would appear from the foregoing that the e.m.f.'s studied herein are characteristics of the respective metals. We believe, for reasons given later, that we determine in our experiments the voltaic contact e.m.f.'s of various metals against steel. Consequently we extended our investigation to many other metals, the results of which are given in Table III. We also give in this table the contact e.m.f.'s for various metals as determined by different previous investigators by other methods. The results of these authors have been expressed with reference to iron by the application, where necessary, of the summation law for contact potentials. E.m.f.'s directed from the second metal towards steel at the surface of contact, and therefore directed from the steel plate to the second metal in the external circuit, are taken to be negative in accordance with the usual practice.

Explanatory.

The metals marked with a † in Table III. were worked with only in the first set of observations. Somehow they were omitted in the second (and so far final) set of determinations, but are given here for the sake of completeness. It may be remarked here again that the maximum values of e.m.f.'s are obtained when the metal is applied to the rim of the rotating steel disk, holding it with the hand and regulating the pressure on the metal and its inclination till large deflexions in the galvanometer are obtained. We have not yet been able to evolve a mechanical method of applying the metal to get the higher voltages, and the deflexions we obtained could not be kept steady for any great length of time. The method adopted to find the maximum value of the e.m.f. for any one metal was to take a large number of observations of deflexions while the metal was kept applied and

Table II.

Showing variation of e.m.f. with speed.

Metal.	E.m.f.'s (millivolts) for different speeds (rev./min.).										Remarks.
	500	600	700	800	900	1000	1100	1200	1300	1400	
Silver.....	—	3·8	—	4·9	—	6·2	—	—	8·0	—	Indifferent polish. Lafay's range.
,, ...	20·0	—	—	33·0	36·0	39·0	44·0	49·0	—	—	Moderate polish. Normal vertical pressure.
,, ...	25·0	—	36·0	38·0	44·0	50·0	54·0	56·0	60·0	—	Better polish than before.
,, ...	—	77·5	—	82·1	—	85·9	88·1	88·4	88·4	87·4	Still better polish. Tangential application.
Copper	—	—	—	6·5	—	8·0	—	9·5	10·4	—	Moderate polish.
,, ...	6·9	9·6	10·6	—	13·8	—	15·9	—	17·6	—	Better polish.
,, ...	32·0	37·0	40·5	41·0	—	41·0	42·0	42·0	42·5	—	Still better polish.

TABLE III.

Giving the potentials for different metals against Steel (or Iron).

Metal.	E.m.f.'s in millivolts as determined by					
	The present authors.	Pellat [1]. Scratched surface.	Pellat [1]. Merely clean surface.	Ayrton and Perry [2].	Erskine Murray [3].	Compton and Richardson [4].
Aluminium	−730					
Magnesium	−617				−870, −1060	−870
Zinc	−553	−640	−540	−600*	−440, −920	−600
Tin	−99	−290	−310	−313*	−390, −520	
Cobalt	−86					
Cadmium	−57					
Lead	−44	−330	−410	−401*	−440, −530	−400
Manganese	−40					
Bismuth†	−20	−40	−70			
Nickel	−13	−10	−90			
Platinum	−8	+380	+320	+369		+260
Antimony	−3	−50	−150			
Arsenic†	+23					
Gold†	+38	+440	+290		+400	
Tellurium	+53					
Copper	+82	+220	+150	+146	−80, +370	
Silver	+123	+400	+350		−20, +70	

[1] British Association Report, 1884, p. 474. Pellat found the potentials of various metals against gold. He used both iron and steel, all the other authors used iron. Values given in the table have been calculated for steel.

[2] Phil. Trans., 1880, pt. i. p. 34. The numbers marked with an asterisk are calculated numbers, others directly determined.

[3] Proc. Roy. Soc. 1898, vol. lxiii. pp. 120–1 & 128. Erskine Murray worked with different metals against gold. Scratching the surface in different ways, he found different potentials. The values given here are the maximum and minimum that can be calculated from those he determined.

[4] Phil. Mag. 1912, xxiii. p. 586. These authors worked between copper and other metals.

attempts made to get the largest possible deflexions, and from these to take a representative value. To give an illustration, the following deflexions were obtained with aluminium, a resistance of 200,000 ohms being in series with the galvanometer and 200 in shunt :—

25, 26, 26, 26, 27, 27, 27, 26, 27,
27, 25, 26, 27, 28, 29, 27, 28, 27.

From these 27 was chosen as the representative value for the deflexion which corresponded to an e.m.f. of 0·73 volt. The number of revolutions of the disk in the above experiment was 1300 per minute.

It has been remarked before that if the pressure with which the metal is applied on to the rim is increased the e.m.f. generated falls off. This was at first thought to be due to the polish of the rim getting spoiled owing to particles of the applied metal getting scratched on to the surface of steel on account of the greater pressure causing excessive friction. It is found, however, that if the pressure is decreased and the metal again applied lightly the deflexions increase again without any fresh polish having been given. Thus in one experiment it was found that the deflexions under the most favourable conditions were 16, 15, 14, 14, 12. When the pressure was increased these fell to 6, 5, 3, 4, 3. On decreasing the pressure the deflexion rose again to 13, 14, 14, 13, 10. This example indicates that the falling off of the e.m.f. was not due to decreased polish. Of course, if the metal is kept applied for a long time the polish does get spoiled and requires renewing to get large deflexions again.

These are Voltaic Contact e.m.f.'s.

The fall of deflexions on increased pressure, but their rising again on decreasing the pressure, and various other characteristics of the phenomenon, can be readily explained if we assume that when any metal is applied to the rim of the revolving disk under conditions to get any deflexion at all there is no actual contact between the two metals, but that there is a fine layer of air separating the two metals, so that the voltaic potential difference between the two is able to manifest itself and to maintain a current in the external circuit. When the pressure is increased this layer of air gets very thin, the conditions approach to those

of an actual contact, and so the e.m.f. also falls; for when two metals are in actual contact they must be at the same potential, except for the very small potential difference which gives rise to the thermo-e.m.f., and which can manifest itself only when there is a difference of temperature between the junctions. The conclusion that in the condition of getting the maximum effect there is no real contact, but that a layer of air separates the two surfaces, gets further support from the observation already mentioned that the contact resistance when the two metals are in relative motion is of the order of a few thousands of ohms. When the disk is stationary and the second metal applied to the rim the contact resistance becomes exceedingly minute.

Controversy regarding the Volta Effect.

Ever since the discovery by Volta in 1802 * of the dry contact electric phenomenon in the case of metals a great controversy has raged as regards the seat of the e.m.f. There is the chemical theory, of which perhaps the greatest exponent is Sir Oliver Lodge †, and according to which the e.m.f. is due to oxidation or, rather, to potential oxidation, and the presence of air is necessary for the exhibition of the effect. On the other hand, the contact theory found its chief exponent in Lord Kelvin ‡, according to whom "the dry volta contact electricity of metals is in the main independent of the character of the insulating medium occupying space around and between the metals concerned in each experiment, and depends essentially on the chemical and physical conditions of molecules of matter in the thin surface stratum between the interior homogeneous metal and the external space" §.

That interest in the subject is still acute is shown by the fact that Professor A. W. Porter chose "Volta Effect" to be the subject of his Presidential Address to Section A

* For an account of Volta's original experiment see the paper on "Contact Electricity of Metals" by Lord Kelvin in Phil. Mag. xlvi. p. 82 (1898).

† See a long report by him to the British Association of 1884, pp. 464–529, "On the Seat of Electromotive Force in the Voltaic Cell," or Phil. Mag. xix. pp. 153–190, 254–280, 340–365 (1885). See also Spiers Memorial Lecture to the Faraday Society (November 1928).

‡ Phil. Mag. xlvi. pp. 82-120 (1898).

§ *Ibid.* p. 103.

of the British Association Meeting of 1928 at Glasgow *, and Sir Oliver Lodge dealt with the same question in the first Spiers Memorial Lecture † to the Faraday Society. It is probably the rapid advances in the field of photo-electricity and thermionic phenomena which have brought this subject of contact potentials into the limelight in recent years. Compton and Richardson ‡ seem to have first realized the necessity of allowing for the contact potential difference in applying Einstein's equation for photoelectric emission, while Millikan § studied the exact manner in which the contact potential difference enters into Einstein's equation. According to Millikan "The mere phenomenon of a free charge remaining on a charged conductor necessitates the existence of a surface force which prevents its escape. It is not a force which in any way impedes the free movement of electricity over or through the conductor, else the body would not act like a conductor. The force acts on the conduction electrons. Even after an electron has escaped from the interior of an atom it cannot escape from the metal until this force is overcome. It is this force which is responsible for about 999-thousandth part of the contact e.m.f.; the other thousandth, measured by the Peltier effect, has a kinetic instead of a static origin" ||.

Characteristics of the present Experiment.

Owing to this static nature of the contact e.m.f. the phenomenon has heretofore almost always been studied electrostatically, the electrometer having been the measuring instrument. In our experiments the effect has been obtained by a relative motion between the metals which are in a dynamic contact, and there is a continuous current in the external circuit, as shown by the galvanometer. Thus the exhibition of the contact e.m.f. by the arrangement described in this paper is fundamentally different from all previous determinations of the effect. There appears, however, to be some similarity of the present arrangements with the Kelvin gravity cell and Kelvin replenisher ¶.

* Brit. Assoc. Rep. xcvii. pp. 21–34 (1928–9).
† Spiers Memorial Lecture to the Faraday Society (November 1928).
‡ Phil. Mag. xxiii. pp. 579–593 (1912).
§ Phys. Rev. vii. pp. 18–32, 355–388 (1916); xviii. pp. 236–244 (1921).
|| *Ibid.* p. 23.
¶ Brit. Assoc. Reports, p. 488 (1884).

Reasons have already been given for the belief that the contact in our case is not an actual metallic one, but that there is a film of air separating the two surfaces. Another fact, mentioned quite early in the paper, namely that the deflexions obtained when freshly polished surfaces are brought in the "dynamic" contact are not so great as when the surfaces have been allowed to stand over for a few minutes, also seems to indicate that a film of air between the metals is necessary for the exhibition of the effect. The process of polishing evidently removes, at least partially, the layer of air adhering to the surface, and the standing over for a few minutes allows the air layer to be formed again. Thus polish plays an important part in our experiment and must be distinguished from Erskine Murray's burnishing *, Pellat's scratching †, or Millikan's preparation of the surface in vacuum ‡. Theirs was an electrostatic method and their aim was cleanliness or changing the orientation of the surface molecules; but in our case a mirror smoothness of the two surfaces, besides cleanliness, is essential for the manifestation of the effect. This extra smoothness probably helps the formation of the separating air film during what has been called the dynamic contact.

This seems to bear out Sir Oliver Lodge's point of view rather than Lord Kelvin's. According to Lodge "wherever electrostatic methods were used, and where electroscope was the instrument of research, contact theorists had it all their own way. . . . But when electric currents were dealt with and the galvanometer was used then the chemists had their turn, and they showed conclusively that no mere contact could maintain a current unless heat disappeared or chemical action occurred" §. In the present experiment we get a current and there is apparently no disappearance of heat, neither is there seemingly any chemical action. We must suppose that the energy of rotation of the disk is responsible for the production of the continuous current.

A Detailed Study of Table III.

It thus seems that the effect described herein is due to contact potential. Lafay's inference that friction between

* *Ibid.* p. 118.
† Pellat's experiments are described in Erskine Murray's paper, p. 113.
‡ Phys. Rev. vii. p. 361 (1916).
§ Brit. Assoc. Report, p. 467 (1884).

the metals was necessary for its exhibition cannot be taken to be correct. Friction has nothing whatever to do with it. In fact all possible attempts are made during the experiment to get rid of friction. Let us then examine our results given in Table III. in detail and in the light of the conclusion that we have measured contact potentials. In the first place, since the voltage given against each metal is the contact potential between the metal and iron, the order of the metals given in Table III., with iron having 0 value, can be regarded as a contact series (" Spannungsreihe "). With this may be compared the usual contact series, which, as given in Winklemann's 'Handbuch der Physik,' † is as follows, retaining only the metals we are concerned with :—

Al—Zn—Sn—Cd—Pb—Sb—Bi—Fe—Cu—
Ag—Au—Te—Pt.

In order to be able to compare our own sequence with the above we rewrite the order of metals as given in Table III. in the above form, putting the metals not found in the above series within brackets :—

Al—(Mg)—Zn—Sn—(Co)—Cd—Pb—(Mn)—Bi*—
(Ni)—Pt*—Sb*—Fe—(As)—Au*—Te*—Cu—Ag.

We see that the two sequences nearly agree but are by no means identical. The metals which are out of place as compared with the series given above have been marked with an asterisk, and are Pt, Au, Te, Bi, and Sb. The last two occupy reversed positions in the two series, but both have negative values in both the series, while Au and Te come after Cu and Ag in Winklemann's series, whereas in our series they come before. Pt is very much out of place, having a small negative value instead of a large positive one.

If now we compare the individual values of the contact potentials as obtained by us with those determined by previous workers using electrostatic methods, we find quite large divergences. Thus, except for aluminium and zinc at one end of the scale and, perhaps, copper and silver at the other, and bismuth in the middle, where the e.m.f.'s determined by us are of the same order of magnitude as, though smaller than, those observed by others,

† Vol. iv. p. 179, 1905 edition.

the rest of the elements show generally considerably smaller values. This may be due to an inherent defect in the method of bringing out the contact e.m.f.'s by the present means. It must be said, though, that it seems likely that by continuing the work higher values of the e.m.f.'s may be obtained. Moreover, the lower values may be due to the second metal not always being in a fit and proper condition to show the full contact e.m.f. Thus, when a metal is rather soft or is brittle or its surface is rough so that it is difficult to make it perfectly smooth, obviously we cannot expect to get very high e.m.f.'s. Then, again, as remarked by Erskine Murray *, the state of the prepared surface and different methods of preparing the surface have a very great effect on the contact e.m.f. of the metals. This is clearly evidenced by the values due to this author given in Table III. According to the treatment given to the surface † his values for a metal like silver show such large variations as to change from negative to positive. It is possible that the negative value for platinum as observed by us, against its universally acknowledged high positive value, may be due to the particular treatment given to the metal in our experiments so far, and it should not be at all surprising if in subsequent repetition of the experiments a positive value for platinum be obtained.

XXXVII. *Electro-Endosmosis in closed Cylindrical Tubes of large Diameter.* *By* B. W. Currie, *Ph.D., Assistant Professor, University of Saskatchewan* ‡.

Abstract.

The velocity of electro-endosmotic flow of a liquid at a point in a closed cylindrical tube of large diameter is shown to be a parabolic function of the distance of the point from the axis of the tube. The velocity along the axis is found to be independent of the diameter. Curves are given from which the endosmotic velocity of water of specific conductivity

* *Ibid.* p. 114, § 2*a*(*b*); p. 119, § 14; p. 122, §§ 18–20.

† Such as scratching with emery and glass papers of different grades, or with file or steel burnishing tools or washleather.

‡ Communicated by Prof. T. Alty, D.Sc., F.Inst.P.

$1{\cdot}0-3{\cdot}0\times10^{-6}$ ohm^{-1} cm.$^{-1}$ along the axis of a silica cell can be read. A value is also given for water of specific conductivity of $1{\cdot}3\times10^{-6}$ ohm^{-1} cm^{-1} in a pyrex glass cell.

Experimental verification is found for the relation, deduced by Debye and Hückel, that the cataphoretic velocity of a particle depends on its shape.

Introduction.

IN a previous investigation by Currie and Alty [1] mobility measurements were taken on gas bubbles, suspended in various aqueous solutions, when they were under the influence of an electric field. The method, developed by McTaggart [2] and Alty [3], consisted in introducing a gas bubble into the liquid contained in a cylindrical silica cell which was rotated about a horizontal axis. The bubble took up a position on the axis and moved along the latter when an electric field was applied between the two electrodes which closed the ends of the cell. The velocity of the bubble was then found by measuring the time for it to travel past a known number of divisions on the eyepiece scale of a long-focus microscope.

The observed velocity is the sum of two velocities, the cataphoretic velocity of the bubble and a velocity due to the return flow of liquid along the axis, caused by the electro-endosmotic flow of the liquid at the walls of the cell. McTaggart [2] and Alty [3] in their work assumed that the latter velocity was negligible since the diameter of their cells (about 2·5 cm.) was large. Burton [4], using his U-tube method of measuring the cataphoretic velocity of colloidal particles, came to a similar conclusion, since varying the diameter of the U-tubes had no apparent effect on the observed velocity. However, Mooney [5] and, more recently, Newton [7] measured the change in velocity of falling oil-drops at different distances from the axes of closed cylindrical tubes, when an electric field was applied between the two ends. They found a parabolic distribution for the liquid velocities, the velocity along the axis being equal and opposite to that at the wall of the tube.

Their results were for cells of glass about one-third the diameter of the silica cell used in the work on gas bubbles, and consequently could not be used for determining the cataphoretic velocities of the gas bubbles.

Theory.

The parabolic distribution of liquid velocities due to electro-endosmosis in closed cylindrical cells can be deduced as follows. Porter [9] has shown that the total difference in hydrostatic pressure P between the ends of the cell is given by

$$P = 2\zeta(V_1 - V_2)K,$$

where ζ is the difference in potential between the layer of ions adsorbed on the wall of the cell and the diffuse layer of ions in the liquid, $V_1 - V_2$ is the longitudinal voltage applied between the ends of the cell, and K the specific inductive capacity of the liquid.

This force presses the liquid against an electrode of the cell and gives rise to an equal and opposite mechanical force which, on account of the rigidity of the electrode, is distributed uniformly over its whole surface. Hence a cylindrical shell of liquid of thickness dr, and at a mean distance r from the axis of the cell of radius R, will be subject to a resultant force

$$\frac{2\zeta(V_1 - V_2)K}{\pi R^2}\{2\pi r\, dr\},$$

tending to move it in a longitudinal direction. This force will be balanced by the viscous forces acting on the inner and outer surfaces of the shell. For steady motion these two forces will be in equilibrium and

$$\frac{2\zeta(V_1 - V_2)K}{\pi R^2}\left\{2\pi r\, dr\right\} = \frac{\partial}{\partial r}\left\{2\pi r l\eta \frac{\partial u}{\partial r}\right\} dr,$$

where l is the length of the cell, η is the coefficient of viscosity of the liquid, and u is the velocity at a distance r from the axis.

Integrating, and assuming that $u = u_0$ when $r = R$ and $u \neq \infty$ when $r = 0$, we have

$$u = u_0 + \frac{2\zeta(V_1 - V_2)K}{4\eta l \pi R^2}\{r^2 - R^2\}.$$

Since the cell is closed, the total flow of the liquid through it is zero or

$$2\pi \int_0^R ur\, dr = 0.$$

On substituting the above value for u, integrating, and solving for u_0 it is found that

$$u_0 = \frac{\zeta(V_1 - V_2)K}{4\pi l\eta} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and hence that

$$u = u_0 \left\{ \frac{2r^2}{R^2} - 1 \right\}.$$

It follows that the distribution of velocities across a closed cylindrical tube is parabolic. Also since $u = -u_0$ when $r = 0$ the velocity along the axis depends essentially on the

Fig. 1.

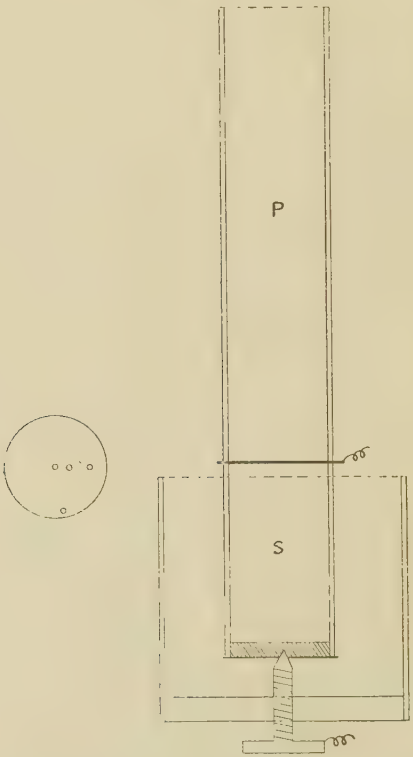


Diagram of cell used to determine the distribution of liquid velocities in cylindrical cells.

ζ-potential between the cell wall and the liquid, and not on the diameter of the tube.

Experimental.

Verification of the Parabolic Distribution of Velocities.

The experimental cell is shown diagrammatically in fig. 1. The part S was the silica cell used in the experiments on gas

bubbles, and the part P, a pyrex tube, 30 cm. in length and open at the upper end. The two were separated by a platinum electrode, having holes about a mm. in diameter at distances $r = 0$, R/3, R/$\sqrt{2}$, and ·85 R from the edge of S. A solid platinum electrode closed the lower end. The two electrodes were connected through a reversing switch to a 160-volt accumulator.

The cell was placed with its axis vertical, and both parts filled with distilled water. A small quantity of an emulsion of *a*-methylnaphthalene in water was poured in at the top. Since this substance has a specific gravity of 1·001, drops up to about 1 mm. in diameter fall very slowly through the water and disturbing effects, caused by pouring them in the cell, disappear by the time they reach the first electrode. A few pass through the openings into S, where the rate of fall of individual drops was measured by means of a travelling telescope and stop watches.

Errors due to convection currents were minimized by surrounding S by a water-cooler with two parallel glass faces. This served a second purpose by preventing distortion of the image of the drop by the curved surface of the cell.

This method made it possible to take observations on drops comparable in size with the gas bubbles used in the previous work. The holes in the electrode fixed definitely the distance of a drop from the axis of the cell, and at the same time limited the number of drops in S, so that disturbing effects due to the charges on neighbouring drops were avoided.

The time for a drop to fall 2 cm. was taken. The electric field was then applied and the time taken for the drop to fall another 2 cm. The same measurements were then taken on a second drop but with the field reversed. This procedure was repeated on two more drops, the electric field being applied over the first 2 cm. and being removed while the drop fell through the second 2 cm. interval. The average of the four changes in velocities was assumed to give the velocity of a drop due to the electric field.

The results for a typical experiment are shown in fig. 2 *a*. Drops about 0·4 mm. in diameter were used. The specific conductivity of the distilled water in the cell was $4{\cdot}8 \times 10^{-6}$ ohm^{-1} cm^{-1}. The observed velocities of the drops in cm.sec./volt/cm. at a temperature of 20° C. are plotted against their distance from the axis of the cell and the resulting curve is a parabola. This is shown more clearly by fig. 2 *b*, obtained by plotting the difference between the velocity along the axis and its value at any other point against the corresponding values of r^2.

The cataphoretic velocity of the drops is given by the observed velocity at $r/\sqrt{2}$, since the endosmotic flow is zero at this distance from the axis. It was found to be always small, and particularly so for large drops. This may be on account of the short period of time in which the surface has to become charged, a result which would be expected from previous observations on gas bubbles [1].

Fig. 2 *a*.

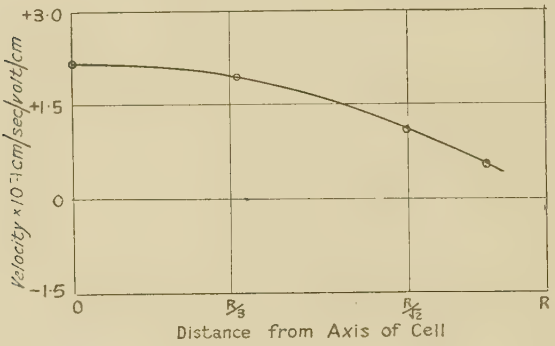
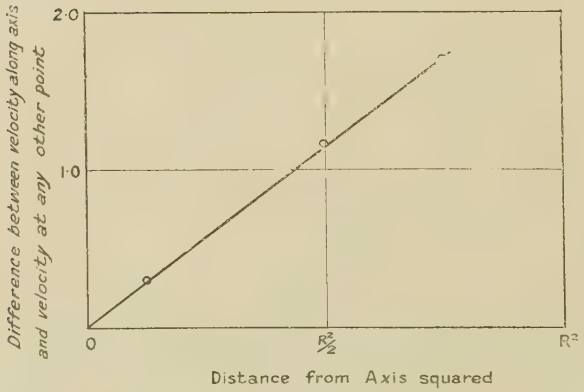


Fig. 2 *b*.



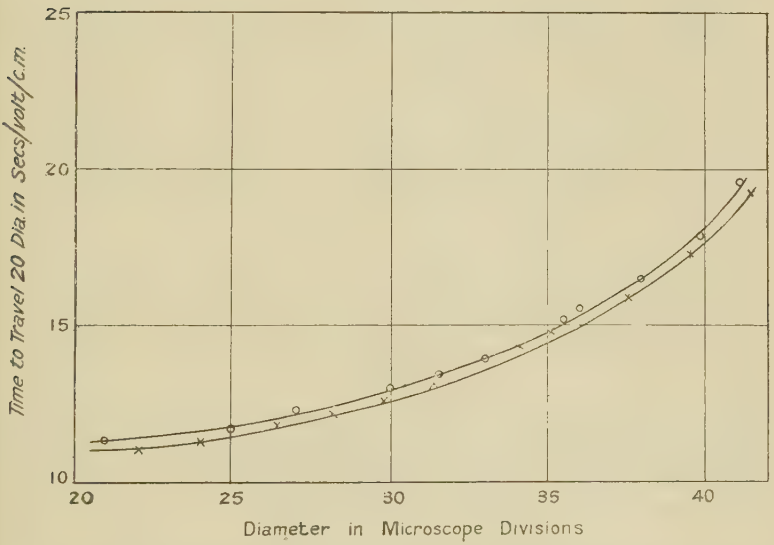
The endosmotic velocity along the axis of the tube is found by subtracting the observed velocity of the drop at the point $r = R/\sqrt{2}$ from the velocity along the axis of the cell. In the case of α-methylnaphthalene the endosmotic velocity is $1{\cdot}2 \times 10^{-4}$ cm./sec./volt/cm. This value substituted for u_0 in equation [1] gives a value of 0·017 volt for the ζ-potential between silica and water.

Velocity along Axis independent of Diameter.

Equation (1) indicated that the endosmotic velocity along the axis was independent of the diameter of the cell. Experiments on air bubbles in rotating cells of slightly different diameters verified this relation over the small range of diameters considered, after a correction had been made to the observed velocities for the effect of the walls and ends of the cells.

Two pyrex cells of diameter 2·6 and 2·2 cm. respectively were used in experiments similar to those described by

Fig. 3.



Alty [3]. Particular care was taken to have similar experimental conditions for successive experiments with the two cells. Each cell was filled with distilled water from the same lot so that both the specific conductivity and the ionic content of the liquid should be the same. Air bubbles of approximately the same size were used for each experiment, and their rate of absorption was practically constant.

The results of a typical experiment are shown in fig. 3, where the time for the bubble to cross twenty microscope divisions under a field of 1 volt per cm. is plotted against the corresponding diameter of the bubble in microscope divisions. It will be observed that the velocity is slightly greater for

bubbles in the cell of larger diameter. For a number of experiments the mean value of the ratio of the velocity of a bubble of diameter 1·4 mm. in the smaller cell to the velocity of a bubble of the same diameter in the larger cell was found to be 0·965.

Viscous forces acting between the walls and the bubble tend to decrease the velocity of the bubble, the decrease being smaller, the larger the diameter of the cell. Bond [8] gives the following relation

$$u_\infty = u\left(1+1{\cdot}6\frac{a}{\mathrm{R}}\right)\left(1+2{\cdot}2\frac{a}{h}\right),$$

between the observed velocity u of a gaseous sphere of radius a, moving along the axis of a cylindrical cell of radius R and length h, and the velocity u_∞ that it would have in one of infinite extent. On substituting the dimensions of the cells in the above relation the ratio between the velocity of a 1·4 mm. bubble in the smaller cell to the velocity that it would have in the larger cell was found to be 0·98, a value very nearly the same as that which was found experimentally.

Variation of Velocity with Specific Conductivity.

It has been shown that the endosmotic velocity along the axis of the cell is given by

$$u = \frac{\zeta(\mathrm{V}_1-\mathrm{V}_2)\mathrm{K}}{4\pi l\eta},$$

where ζ is the transverse potential between the wall and the liquid. Debye and Hückel [9] have shown that the cataphoretic velocity of a small body is given by

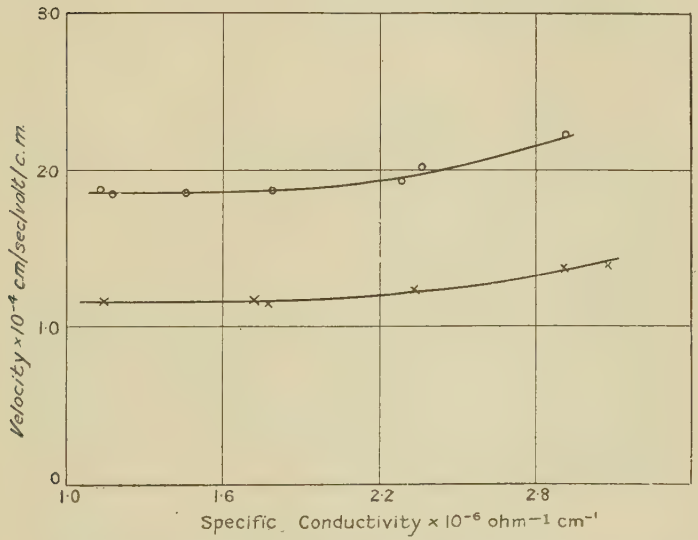
$$u = \mathrm{C}\frac{\zeta(\mathrm{V}_1-\mathrm{V}_2)\mathrm{K}}{l\eta},$$

where ζ in this case is the transverse potential between the body and the liquid, and C is a numerical factor varying with the shape of the body. For a cylinder it has the value of $1/4\pi$ and for a sphere the value of $1/6\pi$. It follows that, if small cylinders of the same material as form the walls of the cell were used in place of the gas bubbles, the cataphoretic and endosmotic velocities would be equal, and the observed velocity along the axis of the cell would be twice the cataphoretic velocity of the body.

The observed velocity, V_1, of a cylinder of paraffin wax, 1·2 mm. in diameter by 3 mm. in length, moving along the axis of the silica cell, is shown as a function of the specific

conductivity of the water used by the upper curve of fig. 4. The variation in the *cataphoretic* velocity, V_2, of the same cylinder with specific conductivity of the water is shown by the lower curve of fig. 4. This was obtained by coating the inside of the silica cell with a thin layer of paraffin wax, similar to that constituting the cylinder, and thus effectively changing the cell from one of silica to one of paraffin wax. The observed velocity of the cylinder of paraffin wax along the axis would then be equal to twice its cataphoretic velocity. The endosmotic velocity of the liquid in the uncoated silica cell will then be equal to $(V_1 - V_2)$. From fig. 4 it appears

Fig. 4.



The endosmotic velocity along the axis of a silica cell is given by the difference between the corresponding ordinates on the two curves: O, observed velocity of a paraffin wax cylinder; X, cataphoretic velocity of the same cylinder.

that the endosmotic velocity is constant and equal to $0{\cdot}69 \times 10^{-4}$ cm./sec./volt/cm. for water having a specific conductivity between $1{\cdot}0$ and $1{\cdot}6 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$.

This result, as well as the Debye-Hückel equation for the cataphoretic velocity, was checked by comparing the cataphoretic velocity of a sphere of paraffin wax of diameter 1·2 mm. with that of the cylinder, as found in the previous experiments. The cataphoretic velocity of the sphere was

obtained by subtracting from its observed velocity in the uncoated silica cell the appropriate value of the endosmotic velocity of the liquid, as indicated by fig. 4. The ratio between this velocity and the corresponding cataphoretic velocity of the cylinder was then compared with the theoretical ratio found by Debye and Hückel [9]. For several experiments the ratio varied from 0·6 to 0·7, a result which is in fair agreement with the theoretical value of 0·66.

Experiments using a pyrex glass bubble in a pyrex cell gave an observed velocity of $1{\cdot}12\times10^{-4}$ cm./sec./volt/cm. This gives a value of $0{\cdot}67\times10^{-4}$ cm./sec./volt/cm. for the endosmotic velocity along the axis of the cell. The bubble was very nearly spherical and had a diameter of 2·46 mm. The specific conductivity of the water which was used was about $1{\cdot}3\times10^{-6}$ ohm^{-1} cm.$^{-1}$.

Summary.

It appears from the above results that :—

(*a*) The electro-endosmotic velocity of the liquid has a parabolic distribution across closed cylindrical tubes of large as well as of small diameter.

(*b*) The velocity along the axis is independent of the diameter of the tube.

(*c*) The velocity along the axis of a silica cell is constant and equal to $0{\cdot}69\times10^{-4}$ cm./sec./volt/cm. for water having a specific conductivity between 1·0 and $1{\cdot}6\times10^{-6}$ ohm^{-1} cm^{-1}.

(*d*) The cataphoretic velocity of a particle depends on its shape, the correct values of the numerical factor appearing in the Debye-Hückel equation being $1/4\pi$ and $1/6\pi$ for a cylinder and a sphere respectively.

References.

(1) Currie and Alty, Proc. Roy. Soc. A, cxxii. p. 622 (1929).
(2) McTaggart, Phil. Mag. xxvii. p. 297 (1914).
(3) Alty, Proc. Roy. Soc. A, cxii. p. 235 (1926).
(4) Burton, ' Phys. Prop. of Colloidal Solutions,' p. 141.
(5) Mooney, Phys. Rev. xxiii. p. 396 (1924).
(6) Porter, Trans. Farad. Soc. xlviii. p. 133 (1921).
(7) Newton, Phil. Mag. ix. p. 769 (1930).
(8) Bond, Phil. Mag. iv. p. 889 (1927).
(9) Debye and Hückel, *Physik. Zeit.* xxv. p. 49 (1924).

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March 9, 1931.

XXXVIII. *On β-transformation.* *By* B. M. Sen, *M.A.*, *M.Sc.*, *Rajshahi College, Bengal**.

THE theory of radioactive transformation on the basis of wave-mechanics was initiated by Gamow (*Zeits. f. Phys.* Bd. li. p. 204, 1928), and by Condon and Gurney (Phys. Rev. xxxiii. p. 127 (1929)). It has been shown that waves can trickle out through potential barriers, and these, considered as packets, may be taken to form α and β radiations. This theory has been worked out in detail by Born (*Zeits. f. Phys.* Bd. lviii. p. 306 (1929)) and Kudar (*Zeits. f. Phys.* Bd. liii. pp. 61, 95, 166, Bd. liv. p. 297 (1929)). In particular, attempts have been made to deduce Nuttall and Geiger's law on the assumption of a complex value for the energy, the physical meaning of which is not clear. Schrödinger waves thus become damped oscillations. But as far as I am aware Heisenberg's objection to the construction of particles out of packets of Schrödinger waves that they tend to spread out in course of time has not yet been met. In the present paper the chances of electrons being emitted from the nucleus as such have been considered. It has been shown that radioactive properties are a direct consequence of increasing atomic numbers.

Taking into account the relativity variation of mass, the equation of motion of an electron may be written in the form

$$\frac{d}{dt}\left(\frac{m_0 v}{(1-v^2)^{1/2}}\right) = \mathrm{F},$$

where m_0 is the rest-mass, v the velocity, and F the impressed force, the velocity of light being 1. This gives

$$\frac{m_0}{(1-v^2)^{3/2}}\frac{dv}{dt} = \mathrm{F}.$$

It is easily verified that for high velocities the consequent acceleration (or deceleration) is a small fraction of its value under the Newtonian law. For example, if v is ·9 the acceleration is about one-twelfth part of its Newtonian value. An electron moving at a high velocity inside the nucleus will therefore be able to surmount a much higher potential barrier under the relativity theory than under the Newtonian theory.

* Communicated by the Author.

We denote by

E the total energy of the particles inside the nucleus,

E′ the minimum energy which enables an electron to jump over the potential barrier,

N the total number of particles,

N′ the number possessing the energy E or more.

The radioactive properties of the substance would depend on the number N′.

Assuming the particles inside the nucleus obey the Fermi-Dirac statistics, we have*

$$N = c\int_0^\infty \frac{E^{1/2}dE}{e^{\alpha+\beta E}+1},$$

$$E = c\int_0^\infty \frac{E^{3/2}dE}{e^{\alpha+\beta E}+1},$$

$$N' = c\int_{E'}^\infty \frac{E^{1/2}dE}{e^{\alpha+\beta E}+1},$$

where c is a constant, α, β are also constants, β being $1/\kappa T$ from thermodynamic considerations. It will be noted that T refers to the temperatures in the nucleus, and not to the temperature of the macroscopic body.

We then have

$$\frac{\partial N}{\partial \beta} = -c\int_0^\infty \frac{E^{3/2}e^{\alpha+\beta E}dE}{(e^{\alpha+\beta E}+1)^2},$$

$$\frac{\partial E}{\partial \beta} = -c\int_0^\infty \frac{E^{5/2}e^{\alpha+\beta E}dE}{(e^{\alpha+\beta E}+1)^2}.$$

Both N and E increase with T.

$$\frac{\partial N'}{\partial \beta} = -c\left\{\frac{E'^{1/2}}{e^{\alpha+\beta E'}+1}\frac{\partial E'}{\partial \beta} + \int_{E'}^\infty \frac{E^{3/2}e^{\alpha+\beta E}dE}{(e^{\alpha+\beta E}+1)^2}\right\}$$

$$= -c\left\{\frac{E'}{e^{\alpha+\beta E'}+1}\frac{1}{\beta}\frac{\partial}{\partial \beta}\left(\frac{E'}{\beta}\right) + \frac{3}{2\beta}\int_{E'}^\infty \frac{E^{1/2}dE}{e^{\alpha+\beta E}+1}\right\}.$$

Putting $\beta = 1/\kappa T$,

$$\frac{\partial N'}{\partial T} = c\left\{\frac{E'T}{e^{\alpha+E'/\kappa T}+1}\left(\frac{E'}{T}-\frac{\partial E'}{\partial T}\right) + \frac{3}{2T}\int_{E'}^\infty \frac{E^{1/2}dE}{e^{\alpha+E/\kappa T}+1}\right\}.$$

N′ therefore certainly increases with T if

$$\frac{E'}{T} > \frac{\partial E'}{\partial T}.$$

* Birtwistle, 'New Quantum Mechanics,' p. 242.

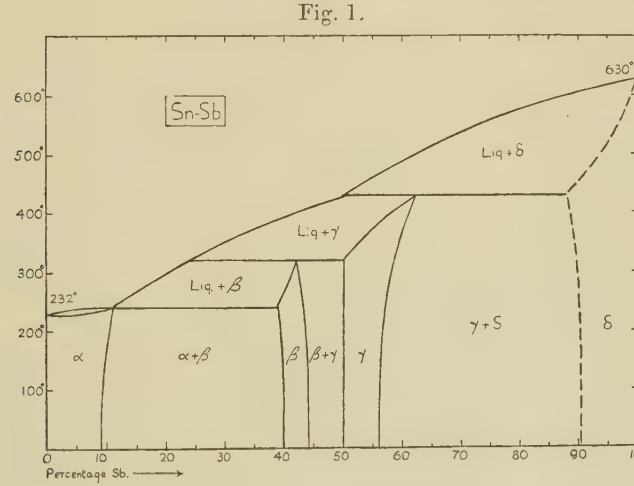
Remembering that N increases with T, we infer that, subject to the above condition, radioactive properties are a direct consequence of increasing atomic numbers. A more definite conclusion will require a more definite knowledge of the potential barrier E′, which is at present lacking.

Rajshahi,
Feb. 18, 1931.

XXXIX. *An X-Ray Investigation of the Tin-Antimony Alloys.* *By* E. G. Bowen, *B.Sc.*, *and* W. Morris Jones, *M.A.*, *M.Sc.*, *F.Inst.P.* (*Physics Department, University College, Swansea*) *.

THE tin-antimony alloys are of considerable industrial importance: they form the base of certain bearing metals and such commercial products as Britannia Metal.

Fig. 1.



The equilibrium diagram of Guertler.

Although a large amount of work has been done on the metallurgical and physical properties of the tin-antimony alloys, the information about them is by no means conclusive, while the crystal structures of the whole system are unknown.

The equilibrium diagram of the system given by Guertler †

* Communicated by the Authors.

† Guertler, 'Metallographie' and 'International Critical Tables,' vol. ii.

is reproduced in fig. 1. At room-temperature it consists of the following constituents :—

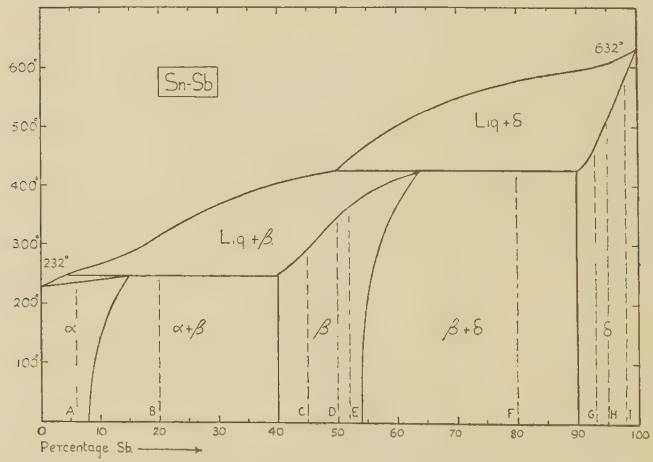
(1) The α phase, a region of solid solution of antimony in tin, up to 9 per cent. of antimony.

(2) The $(\alpha+\beta)$ phase.

(3) The compound Sn_3Sb_2, followed by the β phase, a small range of solution of antimony in the compound, from 40 to 44 per cent. of antimony.

(4) The $(\beta+\gamma)$ phase.

Fig. 2.



The equilibrium diagram of Broniewski and Sliwowski.
The dotted verticals indicate the compositions examined in the present investigation.

(5) The compound SnSb, followed by the γ phase, a solution of antimony in SnSb extending from 50 to 56 per cent. of antimony.

(6) The $(\gamma+\delta)$ phase.

(7) The δ phase, a region of solid solution of tin in antimony up to 9·5 per cent. of tin.

A more recent thermal analysis of these alloys has been made by Broniewski and Sliwowski *, and the diagram they obtained is given in fig. 2.

* Broniewski and Sliwowski, *Comptes Rendus*, clxxxvi. p. 1615 (1928).

At room-temperature this can be divided into five sections :—

(1) The α phase, a region of solid solution of antimony in tin up to 8 per cent. of antimony.

(2) The $(\alpha+\beta)$ phase.

(3) The compound Sn_3Sb_2, followed by the β phase, an extended range of solution of antimony in the compound up to the composition 54 per cent. of antimony.

(4) The $(\beta+\delta)$ phase.

(5) The δ phase, a region of solid solution of tin in antimony up to 10 per cent. of tin.

As a result of this analysis, made in conjunction with measurements of electrical conductivity, thermoelectric power, and other physical properties, they concluded that there was a single intermetallic compound Sn_3Sb_2 ; there was no evidence of the compound SnSb indicated by Guertler.

The electrical resistance of the alloys has been examined in detail by Konstantinov and Smirnov *, and their results are given in fig. 3, together with a curve of thermoelectric powers obtained by Hutchins †.

The curve of electrical resistance gives evidence of the solid solutions about tin and antimony, while in the range 40 to 54 per cent. of antimony there are changes which give some indication of the complex conditions existing in this region. There is a minimum at 50 per cent. of antimony corresponding to the compound SnSb, with maxima on either side, followed immediately by minima at 41 and 54 per cent. of antimony which may be taken as the outer limits of the β and γ phases of Guertler's diagram. Since the peak rising between 50 and 54 per cent. of antimony represents a continuous region of solid solution of antimony in SnSb, the similar peak between 50 and 41 per cent. might represent another *continuous* range of solid solution of tin in SnSb. In this respect there is no evidence for the existence of the $(\beta+\gamma)$ phase given by Guertler ; the β phase must persist from about 41 per cent. of antimony right up to the compound SnSb. Such an extended range of solid solution is found in the diagram of Broniewski and Sliwowski (fig. 2), but this range is considered to extend from a compound Sn_3Sb_2,

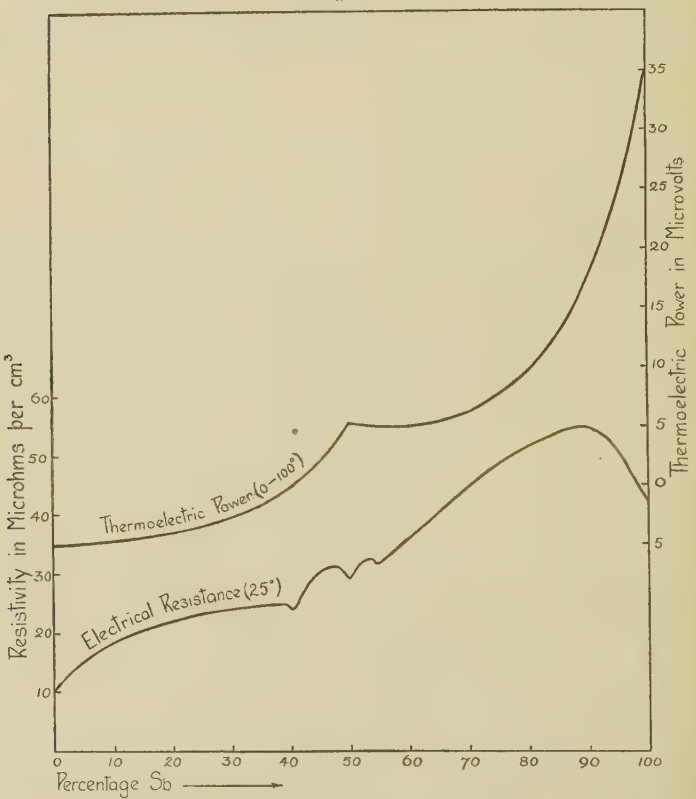
* Konstantinov and Smirnov, Journ. Russ. Chem. Soc. lxiii. p. 1201 (1911).

† Hutchins, Amer. Journ. Science, xlviii. p. 226 (1894).

and not to be on either side of SnSb, as suggested by the curve of electrical resistance.

Further evidence for the existence of the compound SnSb is afforded by the curve of thermoelectric powers included in fig. 3. The curve is smooth and free from discontinuities

Fig. 3.



The resistances and thermoelectric powers of the tin-antimony alloys.

except for the break at 50 per cent. of antimony—at the composition of the compound SnSb.

The microstructures of the alloys have been examined by Stead *, who found excellent cubic crystals of SnSb in the intermediate phases. Many of them were observed to be perfect cubes, having angles of 90° at each corner. They

* Stead, Journ. Inst. Metals, **xxii.** p. 127 (1919).

have also been observed as the hard constituent of the tin-base bearing metals containing a small percentage of antimony.

In view of the conflicting metallurgical data, the present X-ray investigation was concerned mainly with a study of the crystal structures in the region of 50 per cent. antimony. It was expected that if the compounds Sn_3Sb_2 and SnSb existed, they would have distinct crystallographic forms. Solution of tin or antimony in them would produce changes in the lattice dimensions which might enable the limits of solution to be fixed. The intermediate $(\beta+\gamma)$ phase would be a mixture of the two structures. The solid solutions at the tin and antimony ends of the diagram would also be of particular interest, since in early tables of atomic radii atoms of tin and antimony were assigned the same dimensions. Later values show that there is a slight difference, and in this case there should be a change of lattice constant as the pure metal takes the other constituent into solution.

For the purposes of the present investigation a series of nine alloys of suitable composition were prepared, and their crystal structures examined by the X-ray powder method.

Preparation of Alloys.

The preparation of the alloys presented no great difficulty since both tin and antimony have low melting-points. Ingots of some 50 gr. were made and subjected to prolonged periods of annealing, each at a temperature indicated by the equilibrium diagrams.

Certain preliminary results obtained for alloys in the neighbourhood of SnSb were published in 'Nature' *. The general conclusions drawn in that communication have been borne out by subsequent work, but the experimental values given there differ by $\frac{1}{2}$ per cent. from results since obtained after more prolonged annealing. Each alloy for which results are given here was annealed for a period of not less than 200 hours at a temperature within 10° of its melting-point, and then allowed from 4 to 6 hours in which to cool.

The composition and densities of these alloys are given in Table I.

Method of Experiment.

The crystal structures of the alloys were examined by the X-ray powder method. Details of the apparatus used and

* Bowen and Morris Jones, 'Nature,' cxxii. p. 846 (1930).

of the precautions observed to ensure accuracy have been described in previous papers *. Adopting the procedure outlined there, the accuracy of measurement in the present investigation can be estimated as within 1 in 1000.

The copper target used in the X-ray tube gave both K_α and K_β radiations, and faint lines corresponding to the latter appeared on the films. Measurements were made on such lines, so that two results were obtained for the spacing of certain planes. To simplify the tabulation of the results given here the mean of these two values is used.

Results.

A summary of the results is included in Table I., which gives the composition and density, the crystal structure and lattice dimensions of each alloy :—

TABLE I.

Alloy.	Atomic per cent. Sb.	Density in gr./c.c.	Crystal structure.	Dimensions of the unit cell in Å.U.
Tin	0	7·29	Simple tetragonal.	$a_0=5{\cdot}818$; $c=\cdot546$
A	6	7·24	Simple tetragonal.	$a_0=5{\cdot}830$; $c=\cdot546$
B	20	7·12	Simple tetragonal and NaCl structure.	$a_0=5{\cdot}836$; $c=\cdot546$ and $a_0=6{\cdot}126$
C	45	6·93	NaCl structure.	$a_0=6{\cdot}124$
D	50	6·90	NaCl structure.	$a_0=6{\cdot}120$
E	52	6·88	NaCl structure.	$a_0=6{\cdot}115$
F	80	6·74	NaCl structure and face-centred rhombohedral.	$a_0=6{\cdot}110$ and $a_0=6{\cdot}220$; $\alpha=86°\ 30'$
G	93	6·67	Face-centred rhombohedral.	$a_0=6{\cdot}215$; $\alpha=86°\ 36'$
H	96	6·65	Face-centred rhombohedral.	$a_0=6{\cdot}225$; $\alpha=86°\ 54'$
I	98	6·64	Face-centred rhombohedral.	$a_0=6{\cdot}220$; $\alpha=87°\ 0'$
Antimony .	100	6·62	Face-centred rhombohedral.	$a_0=6{\cdot}220$; $\alpha=87°\ 24'$

* Morris Jones and Evans, Phil. Mag. iv. p. 1302 (1927) ; Grime and Morris Jones, Phil. Mag. vii. p. 1113 (1929).

The results confirm the existence of the solid solutions at the tin and antimony ends of the diagram. There is an expansion of the tin lattice and a contraction of the antimony lattice, showing that the atomic radii of these elements are different. In each case the change of lattice dimensions is sufficient to fix the limits of the ranges of solid solution.

The compound SnSb is found to have a sodium chloride structure, which persists alone over the whole range from 40 to 54 per cent. of antimony with some change of lattice constant, showing that there is slight solution of antimony in SnSb and a bigger solution of tin in SnSb extending over the β and $(\beta+\gamma)$ phases of Guertler. The results give no evidence for the existence of the $(\beta+\gamma)$ phase, and are thus in agreement with the deductions from the curve of electrical resistance and with the equilibrium diagram of Broniewski and Sliwowski. But the compound is definitely SnSb, and not Sn_3Sb_2 as these workers thought.

The full X-ray data obtained from films of the nine alloys and the constituent tin and antimony are tabulated in Tables II. to X. Unless stated otherwise, the first column gives the intensity of the lines of the film, the abbreviation St. denoting strong; M. medium; W. weak; and V.W. very weak. The second column gives the Miller indices of the reflecting planes; the third the plane spacings deduced from measurements on the films, and the fourth, plane spacings calculated from the structure found for the alloy.

The α Phase.

The equilibrium diagrams (figs. 1 and 2), show that the α phase is one of solid solution of antimony in tin. The limit of solution is set at 9 per cent. of antimony in Guertler's diagram and at 8 per cent. in the diagram of Broniewski and Sliwowski. The crystal structure of the phase was investigated by means of data from films of pure tin and of alloys A and B, containing respectively 6 and 20 per cent. of antimony.

Data from the film of pure tin are given in Table II. The plane spacings correspond to a simple tetragonal lattice of axial ratio $c=0{\cdot}546$ and lattice constant $a_0=5{\cdot}818$ Å.U., in agreement with the results of Phragmén and Westgren *.

According to Goldschmidt †, the atomic radius of antimony is greater than that of tin, and it is to be expected that

* Phragmén and Westgren, *Zeits. anorg. Chem.* clxxv. p. 80 (1928).

† Goldschmidt, Trans. Faraday Soc. xxv. p. 253 (1929).

solution of antimony in tin will cause an expansion of the tin lattice.

Alloy A (Table III.), containing 6 per cent. of antimony, gave the same system of lines as pure tin, and they were displaced in a direction which showed that there was an

Table II.

Pure Tin.

Intensity.	Plane.	Observed d/n.	Calculated d/n.
St.	100 (2)	2·906	2·909
St.	101	2·781	2·786
W.	110 (2)	2·054	2·057
St.	211	2·013	2·012
W.	301	1·660	1·655
M.	112	1·481	1·481
W.	100 (4)	1·454	1·455
M.	231	1·440	1·438
W.	120 (2)	1·303	1·301
W.	411	1·288	1·290
M.	312	1·204	1·202
W.	431	1·094	1·092
W.	103	1·040	1·041
W.	113	1·023	1·025
W.	123	0·981	0·980
V.W.	100 (6)	0·970	0·970
M.	101 (3)	0·928	0·929
W.	260	0·920	0 920
W.	233	0·886	0·885
W.	541	0·874	0·873
W.	413	0·846	0·846
W.	631	0·836	0·836

Structure:—Simple tetragonal.

Dimensions of unit cell:—a_0=5·818 Å.U.; c=0·546.

expansion of the lattice—an expansion from 5·818 to 5·830 Å.U., with no change of axial ratio. No lines due to the β phase were present on the film, and it follows that this alloy lies within the limit of solution of antimony in tin. To determine the limit it is necessary to consider a composition lying outside this range.

Alloy B (Table IV.), containing 20 per cent. of antimony, gave lines due to both the α and the β phases, and the alloy evidently lies outside the range of solid solution. The lattice constant deduced from lines of the α phase show there is a further expansion to 5·836 Å.U. at the limit of solution.

TABLE III.

Alloy A.

6 per cent. Antimony and 94 per cent. Tin.

Intensity.	Plane.	Observed d/n.	Calculated d/n.
St.	100 (2)	2·915	2·915
St.	101	2·791	2·792
M.	110 (2)	2·066	2·061
St.	121	2·017	2·016
W.	301	1·660	1·658
M.	112	1·508	1·484
W.	100 (4)	1·460	1·458
M.	231	1·431	1·441
V.W.	120 (2)	1·305	1·304
M.	411	1·302	1·293
M.	132	1·204	1·204
M.	431	1·095	1·095
W.	103	1·041	1·043
W.	113	1·026	1·027
V.W.	100 (6)	0·971	0·972
M.	101 (3)	0·929	0·931
W.	260	0·920	0·922
W.	233	0·886	0·887
W.	541	0·876	0·875
W.	413	0·847	0·848

Structure:—Simple tetragonal.
Dimensions of unit cell:—$a_0 = 5{\cdot}830$ Å.U.; $c = 0{\cdot}546$.

The addition of 6 per cent. of antimony to pure tin causes an expansion of the unit cell from 5·818 to 5·830 Å.U., with no change of axial ratio. If the increase follows a linear law, as can be assumed for most solid solutions of restricted range, the lattice constant of tin increases by 0·002 Å.U. for every 1 per cent. of antimony going into solution. The

limiting change is from 5·818 to 5·836 Å.U.—a change of 0·018 Å.U., so that the limit of solid solution of antimony in tin can be fixed at 9 per cent. of antimony, in exact agreement with the value given by Guertler.

The SnSb *Phase.*

The metallurgical and physical data which support the conclusion that the alloy SnSb is a definite compound have

TABLE IV.

Alloy B.

20 per cent. Antimony and 80 per cent. Tin.

Intensity.	Plane.	Observed d/n.	Calculated d/n.
St.	100 (2)	3·055	3·063
M.	**100 (2)**	**2·921**	**2·918**
St.	**101**	**2·794**	**2·795**
St.	110 (2)	2·167	2·166
W.	**211**	**2·019**	**2·018**
M.	111 (2)	1·770	1·769
V.W.	**301**	**1·660**	**1·660**
V.W.	**112**	**1·483**	**1·485**
V.W.	**231**	**1·445**	**1·443**
W.	210 (2)	1·371	1·370
V.W.	211 (2)	1·248	1·250
V.W.	**132**	**1·204**	**1·205**

Structure:—Mixture of simple tetragonal $\begin{cases} a_0 = 5{\cdot}836 \text{ A.U.} \\ c = 0{\cdot}546, \end{cases}$

and NaCl structure, $a_0 = 6{\cdot}126$ Å.U.

NOTE.—Lines of the simple tetragonal lattice of tin are in heavy type.

already been dealt with. The investigations made in this region were therefore concerned with determining the crystal structures of SnSb and examining the ranges of solid solution on either side of it.

The structure of the phase was investigated by means of alloys B, C, D, E, and F, the X-ray data from films of these alloys being given in Tables IV. to VIII.

The results from films of SnSb (alloy D) are given in Table VI., in which the observed plane spacings are the mean of results from three films taken with different

specimens at different times. The agreement between the observed and calculated plane spacings, and between observed and calculated intensities of reflexion, shows that the structure of the compound is of the sodium chloride type. The lattice constants determined for each film separately are 6·118, 6·120, and 6·121 Å.U.; the extreme values differ from the mean by less than 1 in 3000. From these results the lattice constant of SnSb can be fixed at 6·120 Å.U.

TABLE V.

Alloy C.

45 per cent. Antimony and 55 per cent. Tin.

Intensity.	Plane.	Observed d/n.	Calculated d/n.
St.	100 (2)	3·071	3·062
St.	110 (2)	2·174	2·166
M.	111 (2)	1·769	1·768
W.	100 (4)	1·536	1·531
M.	210 (2)	1·373	1·370
M.	211 (2)	1·250	1·250
V.W.	110 (4)	1·081	1·083
M.	100 (6)	1·019	1·021
M.	310 (2)	0·968	0·968
M.	311 (2)	0·921	0·923
V.W.	320 (2)	0·848	0·849

Structure:—Sodium chloride type.
Dimensions of unit cell:—a_0=6·124 Å.U.

The lattice dimensions derived from lines of the SnSb phase for alloys C and B (Tables V. and IV.), containing 45 and 20 per cent. of antimony, are respectively 6·124 and 6·126 Å.U., showing that there is a progressive expansion of the unit cell of SnSb with increasing tin content. The values set the limit of solution of tin in SnSb at 8 per cent. of tin. But the extreme change of lattice constant is hardly outside the limits of experimental error, and this determination of the limit of solution cannot be taken as definite. It is more probable that the limit is at 10 per cent. of tin as given by both equilibrium diagrams.

Alloys E and F (Tables VII. and VIII.), containing 52 and 80 per cent. of antimony respectively, show there is a

decrease of lattice constant with increasing antimony content, from 6·120 Å.U. at the composition SnSb to 6·115 Å.U. when there is 2 per cent. of antimony in solution, and to 6·110 Å.U. at the limit of solution. These figures are sufficient to set the limit of solid solution of antimony in SnSb at 4 per cent. of antimony, in exact agreement with the value given by Broniewski and Sliwowski (fig. 2), but in poor agreement with the 6 per cent. given by Guertler.

Table VI.

Alloy D.

The Compound SnSb.

Intensity. Obs.	Intensity. Calc.	Plane.	Observed. *d/n.*	Calculated *d/n.*
St.	10	100 (2)	3·063	3·060
St.	8·9	110 (2)	2·166	2·164
M.	3·7	111 (2)	1·767	1·767
W.	2·0	100 (4)	1·532	1·530
M.	6·0	210 (2)	1·369	1·369
M.	5·0	211 (2)	1·248	1·250
V.W.	1·7	110 (4)	1·082	1·082
M.	3·8	100 (6) / 221 (2)	1·020	1·020
M.	2·7	310 (2)	0·968	0·968
M.	2·4	311 (2)	0·921	0·923
V.W.	1·7	111 (4	0·885	0·884
.W.	2·0	320 (2)	0·847	0·849

Structure:—Sodium chloride type.

Dimensions of unit cell:—a_0=6·120 A.U.

The changes of lattice constant which occur in the neighbourhood of SnSb are shown in fig. 4, in which the lattice constant is plotted against composition. The diagram emphasises the considerable difference in the conditions which exist on either side of the compound. With increasing tin content, there is an expansion of approximately 0·0006 Å.U. for every 1 per cent. of tin going into solution, and with increasing antimony content a contraction of 0·003 Å.U. for every 1 per cent. of antimony going into solution. Apart from other considerations, the break in this

curve is evidence for the existence of the compound SnSb, with ranges of solid solution on either side.

TABLE VII.

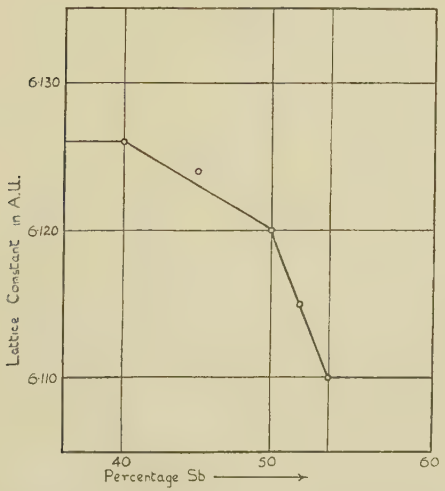
Alloy E.

52 per cent. Antimony and 48 per cent. Tin.

Intensity.	Plane.	Observed d/n.	Calculated. d/n.
St.	100 (2)	3·056	3·058
St.	110 (2)	2·163	2·162
M.	111 (2)	1·764	1·765
W.	100 (4)	1·531	1·529
M.	210 (2)	1·368	1·368
M.	211 (2)	1·248	1·248
V.W.	110 (4)	1·081	1·081
M.	100 (6)	1·019	1·019
M.	310 (2)	0·967	0·967
M.	311 (2)	0·922	0·922

Structure :—Sodium chloride type.
Dimensions of unit cell :—a_0=6·115 Å.U.

Fig. 4.



The changes of lattice constant about SnSb.

An earlier investigation of the crystal structures in this region has been made by Ôsawa *. The structure was thought to be simple cubic, and in consequence the lattice constants given were half the true value. Determinations of the lattice constant were made for three compositions only, and values 6·104, 6·122, and 6·108 Å.U. (after multiplying by two to bring them in line with the present values) were obtained for alloys containing 45, 50, and 55 per cent. of antimony respectively. The dimensions of the unit cell of SnSb and of the alloy containing 55 per cent. of antimony differ from the results of the present investigation by less than 1 in 3000. But the result for the alloy containing 43 per cent. of antimony differs by 1 in 300. From these results Ôsawa concluded that the range of solid solution about SnSb was from 43 to 55 per cent. of antimony—between the compositions examined.

In connexion with his researches into the relation between crystal structure and chemical constitution, Goldschmidt † has made a determination of the lattice constant of the composition SnSb. He gives a value $a_0 = 6{\cdot}130 \pm {\cdot}007$ A.U., which agrees to within 1 in 600 with the present result $a_0 = 6{\cdot}120 \pm {\cdot}006$ A.U.

The Compound SnSb.

Using an atom model based on Schrödinger's wave mechanics, Pauling has calculated the ionic radii of a large number of elements, and applied them successfully to the calculation of the lattice constants of different ionic crystal structures. The arrangement of the constituent atoms of SnSb into a sodium chloride lattice suggests that this compound might be ionic in character, and, perhaps, capable of explanation on Pauling's results.

For tin and antimony, he gives ionic radii :

$Sn^{+4} = 0{\cdot}71$ Å.U.	$Sb^{+5} = 0{\cdot}62$ Å.U.
$Sn^{-4} = 2{\cdot}94$ Å.U.	$Sb^{-3} = 2{\cdot}45$ Å.U.

These values cannot be applied directly to SnSb, as they refer to tetravalent tin and tri- or pentavalent antimony. In the combination of tin and antimony to form SnSb the antimony is most probably electronegative and the tin electropositive. If the antimony is trivalent, then the tin must also be trivalent.

* Ôsawa, 'Nature,' cxxiv. p. 14 (1929).

† Goldschmidt, 'Geochemische Verteilungsgesetze der Elemente,' viii. (1927), and *Berichte Deut. Chem. Gesell.* lx. p. 1263 (1927).

From formulæ given by Pauling * the calculated ionic radii of trivalent tin and antimony are:

$$Sn^{+3}=0{\cdot}75 \text{ Å.U.}, \qquad Sb^{-3}=2{\cdot}45 \text{ Å.U.},$$

which, when built up into a sodium chloride lattice, give a lattice constant $a_0=6{\cdot}40$ Å.U., which is considerably higher than the experimental value $a_0=6{\cdot}12$ Å.U. But the difference is of the same order as found by Pauling himself for compounds made up of large, easily-deformed ions.

However, no great importance can be attached to this theoretical calculation of the lattice dimensions of SnSb. Although a calculated value of the radius of Sn^{+3} can be obtained, it does not follow that this ion actually exists, even in an intermetallic compound, in which elements seldom exhibit their usual valencies.

One important difference between the ionic and the atomic dimensions of tin and antimony is noticeable: the atomic radius of antimony is greater than that of tin, while the ionic radii of electropositive and electronegative antimony are respectively less than the radii of electropositive and electronegative tin. The difference has an important bearing on the solution of tin and antimony by SnSb.

Considering atomic radii, it would be expected that:

(*a*) solution of tin in SnSb—which involves the substitution of tin atoms for antimony atoms—would cause a contraction of the unit cell;

and (*b*) the solution of antimony—involving the substitution of antimony atoms for tin atoms—would cause an expansion of the unit cell of SnSb.

Actually the reverse is found to occur: solution of tin causes an expansion, and solution of antimony a contraction of the SnSb lattice. Evidently the changes are not governed by atomic relations. For their explanation it is necessary to consider the ionic rather than the atomic dimensions of tin and antimony.

The solution of tin in SnSb is the substitution of electronegative tin for electronegative antimony—the amount of electropositive tin remaining fixed at 50 per cent. According to ionic dimensions, this substitution would cause an expansion of the lattice as found in the present investigation. Similarly, in the solution of antimony, substitution of electropositive antimony for electropositive tin would cause a contraction of the lattice, again in accordance with the present results.

* Pauling, Journ. Amer. Chem. Soc. xlix. p. 765 (1927).

It is of some considerable interest that, while atomic radii are found to explain satisfactorily the changes of lattice dimensions of both tin and antimony on solution of the other constituent, in the same system of alloys it is necessary

TABLE VIII.

Alloy F.

80 per cent. Antimony and 20 per cent. Tin.

Intensity.	Plane.	Observed d/n.	Calculated d/n.
St.	100 (2)	3·064	3·055
V.W.	**211**	**2·664**	**2·661**
M.	**110 (2)**	**2·257**	**2·257**
St.	110 (2)	2·165	2·161
W.	**311**	**1·941**	**1·941**
W.	111 (2)	1·762	1·764
W.	**100 (4)**	**1·550**	**1·550**
W.	100 (4)	1·529	1·528
W.	**210 (2)**	**1·419**	**1·419**
M.	210 (2)	1·368	1·367
V.W.	**$2\bar{1}0$ (2)**	**1·353**	**1·355**
V.W.	**211 (2)**	**1·331**	**1·331**
M.	211 (2)	1·248	1·248
V.W.	**110 (4)**	**1·131**	**1·129**
V.W.	110 (4)	1·088	1·080
V.W.	**100 (6)**	**1·033**	**1·033**
M.	100 (6)	1·019	1·018
M.	310 (2)	0·966	0·966
M.	311 (2)	0·921	0·921

Structure:—Mixture of face-centred rhombohedral $\begin{cases} a_0 = 6{\cdot}220 \text{ Å.U.} \\ \alpha = 86° 30', \end{cases}$ and Sodium chloride structure, $a_0 = 6{\cdot}110$ Å.U.

NOTE.—Lines of the face-centred rhombohedral lattice of antimony are in heavy type.

to use ionic radii to explain the changes of lattice constant of SnSb on solution of tin or antimony.

In passing, it should be observed that SnSb appears to be the only intermetallic compound having a sodium chloride structure which is capable of taking the constituent metals

into solution. This is probably due to the close relationship between tin and antimony: they lie next to one another in the periodic table, while either metal exists in both electronegative and electropositive states—both have distinct acidic and basic properties. The combination of circumstances is such that the substitution of tin for antimony, or of antimony for tin, takes place very readily in the lattice of SnSb.

The δ Phase.

According to both equilibrium diagrams (figs. 1 and 2), there is solid solution of tin in antimony up to 10 per cent. of tin. Examination of the equilibrium diagrams of the antimony alloys shows that it is incapable of dissolving any other metal to this extent with the exception of bismuth, which has the same face-centred rhombohedral structure as antimony. It is possible that antimony takes into solution very small quantities of copper, silver, gold, and lead, but the existence of these small ranges of solid solution is by means certain. Earlier X-ray investigations of the systems Cu–Sb * and Pb–Sb † made in this laboratory have shown that not more than 0·5 per cent. of either copper or lead is soluble in antimony. It is probable that the solution in antimony of any other metal (excepting Bi and Sn) does not exceed this amount.

Since antimony has a face-centred rhombohedral structure, it would be expected to dissolve other metals only with difficulty. The solution of as much as 10 per cent. of tin is surprising, and the only apparent reason for it is again the relation between tin and antimony. It was mentioned that they are placed next to one another in the periodic table, having almost identical atomic dimensions.

When determining the limit of a small range of solid solution by X-ray methods we have assumed that any change of lattice constant is a linear function of the composition. The present case is exceptional and of particular interest, since no previous example of solution into a rhombohedral lattice appears to have been examined in detail. Accordingly three alloys G, H, and I, were prepared containing, respectively, 93, 96, and 98 per cent. of antimony, all lying within the δ phase. From the examination of films of these alloys and of pure antimony it has been possible to show how the lattice dimensions of the rhombohedral cell of antimony change with the amount of tin in solution.

* Howells and Morris Jones, Phil. Mag. ix. p. 993 (1930).

† Solomon and Morris Jones, Phil. Mag. x. p. 470 (1930).

The X-ray data for pure antimony are given in Table X. It corresponds to a face-centred rhombohedral structure having lattice constants $a_0 = 6{\cdot}220$ Å.U. and angle $\alpha = 87° 24'$. The side of the unit cell agrees to within 1 in 1000 with the results of Persson and Westgren *, and the angle is identical.

The data from films of alloys G, H, and I are given collectively in Table IX. Solution of tin causes no perceptible

TABLE IX.

Alloys G, H, and I.

Plane.	93 per cent. Sb.		96 per cent. Sb.		98 per cent. Sb.	
	Obs. d/n.	Calc. d/n.	Obs. d/n.	Calc. d/n.	Obs. d/n.	Calc. d/n.
100 (2)	3·093	3·097	3·114	3·104	3·100	3·102
110 (2)	2·253	2·254	2·257	2·253	2·246	2·250
$\bar{1}10$ (2)	2·131	2·131	2·145	2·140	2·139	2·140
$\bar{1}11$ (2)	1·756	1·756	1·765	1·763	1·763	1·762
100 (4)	1·549	1·549	1·553	1·552	1·552	1·552
210 (2)	1·416	1·417	1·417	1·418	1·413	1·416
$\bar{2}10$ (2)	1·354	1·355	1·361	1·361	1·361	1·361
$\bar{2}\bar{1}1$ (2)	1·253	1·253	1·256	1·256	1·257	1·256
$\bar{2}11$ (2)	1·231	1·230	1·237	1·236	1·237	1·236
100 (6)	—	—	1·032	1·034	1·033	1·034
$\bar{2}21$ (2)	—	—	1·012	1·012	1·012	1·012
310 (2)	—	—	0·996	0·997	0·994	0·996
311 (2)	—	—	0·966	0·968	0·967	0·966
$3\bar{1}1$ (2)	—	—	—	—	0·933	0·931
$\bar{1}11$ (4)	—	—	—	—	0·881	0·881
Dimensions of unit cell.	$a_0 = 6{\cdot}215$ Å.U. $\alpha = 86° 36'$.		$a_0 = 6{\cdot}225$ Å.U. $\alpha = 86° 54'$.		$a_0 = 6{\cdot}220$ Å.U. $\alpha = 87° 0'$.	

change of the intensity of the reflexions, and in this table the usual column of intensities has been omitted.

The dimensions of the unit cells of these three alloys and of pure antimony are:

Alloy G., 93 per cent. Sb.: $a_0 = 6{\cdot}215$ Å.U.; $\alpha = 86° 36'$.
Alloy H., 96 per cent. Sb.: $a_0 = 6{\cdot}225$ Å.U.; $\alpha = 86° 54'$.
Alloy I., 98 per cent. Sb.: $a_0 = 6{\cdot}220$ Å.U.; $\alpha = 87° 0'$.
Pure Sb., 100 per cent. Sb.: $a_0 = 6\ 220$ Å.U.; $\alpha = 87° 24'$.

* Person and Westgren, *Zeits. Phys. Chem.* cxxxvi. p. 208 (1928).

The edge of the unit cell deduced for alloys G and H differs from those of the other alloys by less than 1 in 1000, and, within experimental error, it can be said that there is no change of edge on solution of tin. There is, however, a decrease of the angle of the rhomb, indicating that the volume of the antimony cell diminishes as tin goes into solution. The result is in agreement with the fact that the atomic radius, or the atomic volume of tin, is less than that of antimony.

TABLE X.

Pure Antimony.

Intensity.	Plane.	Observed d/n.	Calculated d/n.
M.	100 (2)	3·107	3·104
M.	110 (2)	2·246	2·245
M.	$\bar{1}10$ (2)	2·145	2·148
W.	311	1·934	1·931
W.	111 (2)	1·874	1·875
M.	$\bar{1}11$ (2)	1·766	1·766
W.	100 (4)	1·552	1·552
M.	210 (2)	1·411	1·412
M.	210 (2)	1·364	1·364
W.	$2\bar{1}1$ (2)	1·259	1·259
W.	211 (2)	1·241	1·241
V.W.	$\bar{1}10$ (4)	1·076	1·075
V.W.	100 (6)	1·032	1·033
V.W.	221 (2)	1·012	1·015

Structure :—Face-centred rhombohedral.

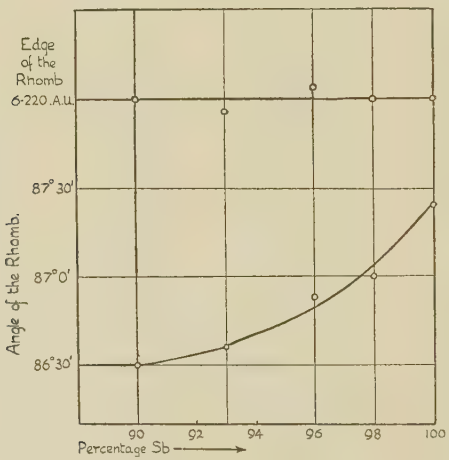
Dimensions of unit cell :—a_0=6·220 Å.U.; α =87° 24′.

At the limit of solution the side and angle of the rhombohedron are a_0=6·220 Å.U. and α=86° 30′ respectively. These values were deduced from lines of the β phase on the film of alloy F (Table VIII.), containing 80 per cent. of antimony and lying outside the region of solution of tin in antimony. If we assume the limit of solution is at 10 per cent. of tin, as given by the equilibrium diagrams, a curve (fig. 5) can be drawn showing how the angle α changes with composition.

The angle of the rhomb deduced from alloy F, and inserted at 90 per cent. of antimony, fits in with the curve. This justifies the assumption that the limit of the δ phase is at this composition. In this respect the present investigation gives evidence that the limit of solid solution of tin in antimony is at 10 per cent. of tin.

A preliminary determination of the lattice-edge of antimony gave a value $a_0 = 6{\cdot}235$ Å.U. but after annealing the same specimen for 200 hours at a temperature near its melting-point, a steady value of the lattice constant 6·220 Å.U. was obtained. It was also found that the edge of the unit cell for alloys of high antimony content, containing from

Fig. 5.



The changes of lattice dimensions of antimony on solution of tin.

90 to 100 per cent. of antimony, were liable to vary considerably with heat-treatment. After the usual period of annealing (200 hours), some of these alloys gave a value as high as $a_0 = 6{\cdot}235$ Å.U. Only after annealing for up to 400 hours did the results become consistent, and constant about the value $a_0 = 6{\cdot}220$ Å.U.

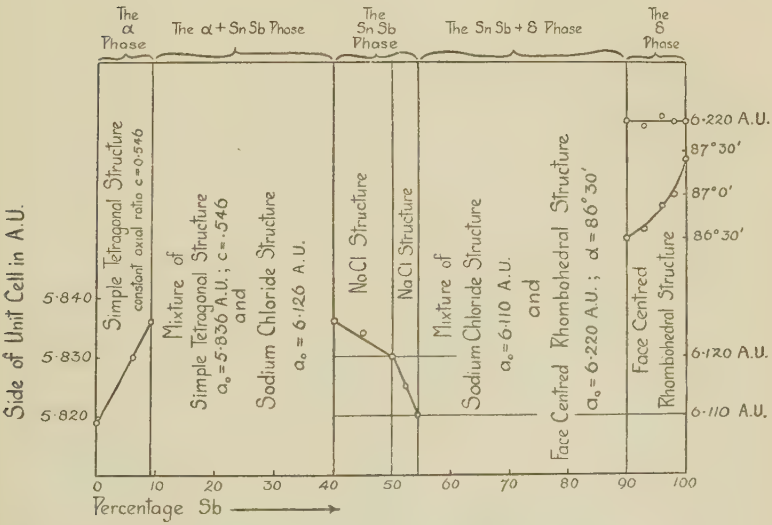
To conclude, it would be interesting to trace the evolution of the crystal structures of the alloys with increasing antimony content.

The structure of pure tin is simple tetragonal, having a lattice constant $a_0 = 5{\cdot}818$ Å.U. and axial ratio $c = 0{\cdot}546$. The addition of up to 9 per cent. of antimony causes an expansion of the unit cell to $a_0 = 5{\cdot}836$ Å.U , with no change

of axial ratio. This is the α phase of solid solution of antimony in tin. Further addition of antimony causes no change of this structure, but the sodium-chloride lattice of SnSb appears until at 40 per cent. of antimony the whole structure is of the sodium chloride type. At this composition the SnSb phase begins.

The changes of lattice constant within this phase, drawn in fig. 4, show that there are two distinct regions of solid solution on either side of SnSb. There is a solid solution of tin in SnSb from the composition 40 to 50 per cent. of antimony, and solution of antimony in SnSb from 50 to 54

Fig. 6.



The crystal structures of the tin-antimony alloys.

per cent. The solution of 10 per cent. of tin causes an expansion of the unit cell from 6·120 to 6·126 Å.U., and the solution of 4 per cent. of antimony, a contraction from 6·120 Å.U. to 6·110 Å.U.

With further addition of antimony the face-centred rhombohedral structure of antimony appears, and the mixture of two phases persists until the composition 90 per cent. of antimony, at which the phase begins.

The δ phase is a region of solid solution of tin in antimony, within which there is no change of the edge of the rhomb, but an increase of angle with increasing antimony content,

from 86° 30′ at the limit of solution, to 87° 24′ for pure antimony. The lattice dimensions of pure antimony are $a_0 = 6{\cdot}220$ Å.U. and $\alpha = 87° 24'$.

We wish to thank Professor E. J. Evans for facilities for carrying out this work and for his interest during its progress.

April 27th, 1931.

XL. *Tears of Strong Wine.* *By* Max Loewenthal *.

[Plates VIII. & IX.]

1. *Preliminary Remarks.*

IT is a matter of common observation that a strongly alcoholic liquid, such as port wine, exposed to the air in an open glass vessel, creeps up the sides of the vessel in the form of a fine film which terminates in a thickened marginal "roll," and that this "roll" becomes at intervals studded with drops which grow in size until they detach themselves and return to the mother liquid in the form of "tears."

The explanation of this phenomenon put forward by James Thompson, and quoted by J. C. Maxwell and Lord Rayleigh in the 'British Encylopædia' under "Capillary Action," is that evaporation of alcohol renders the surface-region of the marginal or ascending film more aqueous than that of the bulk of the liquid because there is but little *reserve* alcohol in the former, whereas everywhere else the loss of alcohol suffered by evaporation is quickly made good by diffusion from the deeper strata. The surface-tensions at the free surface of the marginal portions are, therefore, greater than that of the stronger alcohol of the central portion, with the result that the liquid is continually dragged up the sides of the vessel, and, there accumulating, some of it descends from time to time as "tears."

It has for some time appeared to me that this explanation, although perhaps good as far as it goes, is not adequate to account for all the facts, and that any full explanation ought to take into consideration two further possibilities :—

(1) The postulated dilution of the alcohol in the marginal film might result from absorption of water-vapour from the air as well as from loss of alcohol by evaporation.

* Communicated by the Author.

(2) I have long held that the view put forward in this paper, more than a century ago, by John Leslie, and more recently by Ramsden, that the layer of liquid next the walls of any solid which it "wets" is the seat of an interface pressure, or, as Ramsden prefers to call it, a "negative surface tension." If this is correct, the possibility exists that some, or even all, of the liquid which goes to form the tears might be thrust up by a driving force; in other words, that it is not drawn upwards by surface-tension, but is driven upwards by interface-pressure.

I have accordingly experimented with a considerable variety of different systems in order to ascertain what conditions are essential for the formation of tears analogous to those observed with strong wine.

2. *Water-miscible Volatile Liquids.*

The formation of tears is best studied in clock-glasses, 3 to 6 inches in diameter. These were prepared for use by treating them with strong caustic soda, then washing under the tap, finally with distilled water, and drying, face downwards, over blotting-paper. The physical purity thus obtained was found sufficient to obtain consistent results. Control experiments made in vessels cleaned in the orthodox manner did not appreciably differ in their results.

The "weeping" of volatile liquids is favoured by all conditions which increase evaporation, such as rise of temperature, air-currents, or free exposure to the surrounding air. Conversely, "weeping" is retarded by cold weather or by restricting communication with the outer air, and ceases altogether in closed vessels.

That the layer which forms the free surface of the "weeping" liquid is throughout its whole extent in a state of motion can be demonstrated by powdering the surface of a 50 per cent. alcohol-water mixture with sublimated sulphur. This reveals a continuous centrifugal surface-current which extends from the centre of the free surface of the mother liquid to its periphery, and through the ascending film right up to the marginal "roll" to which it supplies the liquid used in the formation of tears. It is probably this observation which made former workers in this field regard the formation of tears as a surface phenomenon pure and simple; but while local differences of surface-tension may account for the transportation of liquid from the central to the peripheral portions of the surface, it is difficult to see how such differences can lead to a considerable enlargement of the free

surface and the liquid-solid interface, for surface-tension tends to contract, not to expand, surfaces.

Thompson's interpretation is based on the presence of water in the alcoholic liquid, but it is easy to show that water in solution is quite immaterial. *Absolute alcohol exposed to the air gives a prompt reaction.* The addition of water, far from promoting the weeping, makes it more sluggish and less copious.

If the air in a conical flask containing a mixture of 70 per cent. alcohol and 30 per cent. water tinged with methylene blue is being continually exhausted by water-suction, there is brisk evaporation of surface alcohol, and all the conditions for the formation of tears required by Thompson's interpretation are given, but the mixture remains inert, and no tears are formed.

The result is equally negative if a brisk current of air which has been previously deprived of every trace of moisture by being passed through a number of drying-bottles is conducted over the mixture contained in the flask.

The first clue towards an elucidation of the phenomenon is obtained by conducting through the flask air which has not been previously dried. If this is done, the edge of the liquid, now recognizable as a blue ring of moisture, can be seen slowly creeping upwards.

At the same time, drops develop within this ring which grow until, after reaching a certain size, they slide slowly back into the mother liquid. Their downward flow is impeded by an invisible current flowing in the opposite direction as a fine film to feed the drops which form at its upper margin. If the outer air previous to entering the flask is saturated with moisture by being made to pass through water, the circular array of tears is formed as high as 5 cm. above the general level of the liquid, and weeping is profuse.

It seems, therefore, that the water present in the volatile liquid plays a neutral part, while atmospheric moisture is an important adjuvant.

The same results can also be obtained if, instead of ethyl-alcohol, other liquids are used which are at the same time volatile and miscible with water in all proportions. *Methyl-alcohol* and *acetone*, pure or mixed with water, are excellent substitutes ; so also is *glacial acetic acid*, which satisfies the same conditions. This class of volatile liquids yields tears as long as they are exposed to the air and the amount of absorbed water does not exceed a certain limit.

3. *Simple and Mixed Volatile Liquids.*

The degree of weeping of *simple* volatile liquids exposed to the air depends on their affinity for water. It is greatest in those which are miscible with water in all proportions, slight in those which are miscible in small proportions, and absent in all those liquids which are soluble in water in traces or not at all. Sulphuric ether, for instance, whose solubility is 1 : 10, forms a film, but, instead of flowing tears, only minute droplets at the upper margin of the film. Paraldehyde, which has the same solubility, but is much less volatile, does not even form a film. *Acetic ether* and *chloroform*, highly volatile, but of low solubility, are as inert as benzene and as the whole group of pure volatile liquids which are quite immiscible with water.

As would be expected, the reaction in its most intense form is seen in mixed liquids. Since both volatility and solubility in water are essential conditions for the formation of tears by pure liquids exposed to the air, it is possible to obtain excellent results by choosing and mixing two liquids one of which is highly volatile while the other has a great affinity for water. Thus weeping is considerably increased by adding *sulphuric or acetic ether to alcohol or acetone.*

It suffices if only one of the liquids is volatile. In this way many weeping liquids can be formed of components which by themselves are perfectly inert. Such mixtures are *chloroform c. phenol, acetic ether c. sulphuric acid, acetic ether c. paraldehyde, and many others.* Even paraldehyde c. phenol, both inert and neither of them very volatile, gives a weeping mixture.

4. *Liquid and Solid Solutes.*

Further experiments showed that the binary systems just mentioned develop tears not only on free exposure to the air, but likewise, though in a slightly lesser degree, in a dry atmosphere. It was therefore important to find out whether an affinity for water of at least one of the components was at all necessary, or whether it would not be possible to find substances lacking this property which could take the place of the water-miscible liquid.

Experiments conducted with this end in view revealed the fact that *there is probably no volatile liquid which cannot be made to produce a marginal film and tears in union with other liquid or solid substances in the complete absence of water or water-vapour.*

In order to perform clock-glass experiments in dry air, a vertical tube with stopcock and cylindrical funnel is let into the centre of the lid of a desiccator. A clock-glass is placed inside underneath the tube through which the mixture to be examined is admitted as soon as the confined space can be assumed to be free of moisture. The stopcock is then left open to render evaporation possible, and the funnel is filled with fused calcium chloride.

(*a*) Pure alcohol or glacial acetic acid give no tears under these conditions, as is to be expected, but, as already mentioned, a clear mixture containing one part of phenol to two of chloroform * gives the reaction almost as well as on free exposure. This shows that phenol has another function beside that due to its affinity for water. The same holds good for other mixtures of this class.

(*b*) Weeping mixtures can be obtained by combining two liquids both of which are almost or entirely immiscible with water. The liveliest reaction I have ever seen is given by a mixture consisting of equal parts of benzene and petroleum ether. The moment this mixture touches the glass it spreads itself out almost simultaneously over a large area, and large tears are formed in great abundance.

Benzene by itself is inert and petroleum ether almost so, while together they give the reaction in an extreme form. *Petroleum ether c. acetic ether* also gives a very active mixture.

Not every combination of volatile liquids gives the reaction. *Chloroform c. benzene*, for instance, is quite inert.

It may be stated that no simple volatile liquid which is in a state of absolute purity exhibits the phenomenon. Terebene, for instance, gives a large film and distinct weeping, but is not, in the chemical sense, a simple liquid.

(*c*) *Every simple volatile liquid can be rendered active by* dissolving in it some appropriate solid substance.

The reaction is seldom so lively as that given by mixed liquids, but quite distinct. The addition of common *resin, guajac resin*, *Canada balsam*, *or dragon's blood* to any volatile liquid has this effect. So have the whole class of aniline dyes as far as they are soluble in the liquid to be examined. The addition of a dye has the further advantage of rendering the extreme margin of the ascending film visible, and disclosing details of its formation.

* This mixture becomes clear after standing for 3 or 4 hours.

Other useful solids are *camphor*, *menthol*, and *thymol*, because of their general solubility. Acetic ether is rendered highly active by the addition of 5 to 10 per cent. of *resorcin*, sulphuric ether by *salicylic acid*, which is easily soluble in it.

5. *A Driving Force.*

The following observations do not exclude the possibility that differences of surface-tension as postulated by J. Thompson participate in the transportation of liquid and the production of tears, but they are held to demonstrate the existence of a driving force which enlarges the area of contact between solid and liquid. It is my contention that this driving force is identical with the interfacial pressure postulated by John Leslie, which, according to him, is the cause of the rise of liquids in capillary tubes. It is claimed for this pressure that it is present in the liquid layer in the immediate neighbourhood of the solid, and that it acts in all directions parallel to the solid surface. If this reservation be borne in mind, it will be safe to refer to it in future as "interface pressure."

That the ascending sheet of liquid moves against the trend of gravity under the influence of a force which in its effects is strongly suggestive of an "interface-pressure" is borne out by the following observations :—

(*a*) *The mode of its formation.*—This can be observed quite distinctly in liquids deeply coloured by an aniline dye or dragon's blood. The first thing to be noticed is the formation of fine linear spurts of liquid, with a quickly growing droplet at the end of each, all round the rim of the meniscus (Pl. VIII. fig. 1).

The linear shoots then broaden out and the drops increase in size until they coalesce into a fenestrated film (Pl. VIII. fig. 2).

If the reaction is slow, as in chloroform c. aniline violet (under cover above water to retard evaporation), the drops, connected by a short neck with the margin of the liquid, remain separate, although they grow to a considerable size (Pl. IX. fig. 3).

In quickly growing films second shoots appear on the drops before these have become confluent (Pl. IX. fig. 4). Criss-crossing with each other they often give rise to elaborate patterns.

(*b*) With the help of a magnifying lens, and while the reaction is going on, occasional undissolved particles of the

dye can be seen travelling along the thin stem and collecting in the distal half of the terminal drops.

That these particles are carried along by an interfacial current may be concluded from the fact that *the "floor" of the proximal half of the drop is swept clean and is divided from the opaque distal half by a straight line.*

This interfacial migration of solutes likewise suggests the existence of a driving force.

(*c*) It is possible to hasten or revive the reaction by blowing on the weeping liquid. Every time this is done a fresh ascending current with a well-defined upper edge rises from the rim of the liquid and advances rapidly upwards, being thus superimposed on the old film. By blowing on the liquid repeatedly at short intervals a series of ascending currents can be started, and it often happens that a fresh wave travelling with exceptional rapidity overtakes the advancing edge of the preceding wave. This phenomenon can be best studied with a 5 per cent. solution of iodine in one part of alcohol to two or three of ether, using as vessel a large porcelain dish.

There is no doubt that *the rate of progress of the lower part of the old film is independent of that of the upper part*, which proves that the advancing edge is not, or at any rate not appreciably, drawn upwards by surface-tension.

(*d*) The same arrangement can be used to demonstrate another pressure phenomenon. The outer margin of the ascending film is defined by a thick dark line containing iodine in concentrated solution from which deeply dyed tears detach themselves at intervals. If, now, the dish is tilted in different directions, the dark line can be seen to move bodily upwards towards the rim of the vessel long before it is reached by the edge of the solution—a clear proof *that it is not drawn, but driven* upwards.

The Marginal Film.

The thickness of this film, as a rule, exceeds that of soap-bubbles, for iridescence is seen only exceptionally, but it is thin enough, nevertheless, to be discernible only by the gloss it gives to the surface of the glass. It cannot be more than a few micro-millimetres in depth. The film is the direct continuation of the extreme edge of the concave meniscus, and consists of two layers :

(1) the inner layer which is in contact with the surface of the solid, and

(2) the outer layer, which forms the free surface of the film and is continuous with the free-surface layer of the mother liquid.

(*a*) It is important to remember that these two layers, which are widely apart in the mother liquid, are in such close proximity in the extreme rim of the meniscus and in the marginal film that *neither of them can suffer a change in its chemical composition without a corresponding change taking place in the other.*

Evaporation produces a change of composition not only in the outer layer, but, secondarily, and almost simultaneously, in the inner layer. Diffusion over such a minute distance is bound to run its course in an exceedingly short span of time. Nor can absorption by the outer layer, if the liquid is water-miscible, of molecules of water from the air take place without immediately producing a chemical disturbance in the subjacent inner layer.

It is self-evident that evaporation can produce a change of composition in composite liquids only.

Simple volatile liquids, as has already been stated, cannot by themselves produce tears. The composition of the outer layer may be changed by evaporation or absorption in compound liquids ; in simple liquids by absorption only.

Ascending films or tears can be induced by the absorption of other gases than water-vapour. If two watch-glasses, one containing some acetic ether, the other glacial acetic acid, are placed side by side, exposed to the air, it is the acid which develops tears, while the ether remains inert : but if they are placed side by side under a glass cover, an *iridescent* film and, later on, tears are formed in the vessel containing the ether, while the heavier liquid remains inert. Of two watch-glasses under cover containing petroleum ether and benzene respectively, the former develops a non-iridescent film and tears, while the benzene remains inert. Such instances of weeping by absorption can be multiplied at will.

A few words may not be out of place to meet an obvious objection to the possibility of a movement *en masse* of the liquid interface layer which forms the inner layer of the film. This layer is in a state of adsorption, and must be expected to share with other interfacial layers of the same kind the property of being more viscous than the rest of the liquid. This viscosity, with the resulting internal and external friction, must be regarded as an obstacle to the ready flow of the interfacial layer relative to the surface of the solid. It must, however, be borne in mind that, owing to the constant interchange of molecules already referred to between the inner

and outer layer, the marginal film is throughout in a state of molecular unrest, and it is suggested that the incessant disturbance communicated to the molecules of the inner layer as a consequence of evaporation or absorption at the free surface has the effect of facilitating the advance of this layer.

(*b*) There is another important aspect to the thinness of the marginal film. An old experiment shows that, if a submerged glass slide is vertically withdrawn from water, the surface of which is powdered with lycopodium, the particles hasten from all sides towards the moving slide and adhere to it, as if the surface formed a coherent skin. The surface-layer of water adheres to the interfacial layer of the water which is in contact with the glass, and is carried along with it. The centrifugal motion of the surface-layer of weeping liquids admits of the same explanation. Owing to the exceeding thinness of the ascending film, a primary movement of its inner layer must be communicated to, and shared by, its outer or surface-layer. This statement does not, of course, exclude the possibility that the movement of the surface-layer may in part be due to differences of tension between the central and the peripheral parts of the free surface.

7. *The Behaviour of Drops of Weeping Liquids.*

It must be borne in mind that a considerable amount of work is performed in the course of the reaction. If the reaction is lively the original surface-area may be enlarged six times and more. This means that the original potential energy of the free surface, provided that its intensity is not lowered, is increased an equal number of times.

The difference between the original and the resulting surface areas is still more conspicuous if very small amounts of liquids are used. *Highly active weeping mixtures do not form stable drops on solids.* A small drop (0·03 cm.^{3}) of benzene c. petroleum ether on glass expanded almost simultaneously to 5 cm.^{2} of free surface. An enormous increase of potential energy !

This rapid expansion of drops into a thin film reminds one of the behaviour of drops of oil on the surface of water. But whereas the oil, by spreading, reduces the total amount of surface energy, the expansion of a drop of volatile liquid on glass means an increase of the potential energy, *of the free surface at least*, to about fifteen times its original amount. It is a legitimate conclusion that the energy required for this

expansion is liberated at the interface by the contact between the solid and the liquid, and *that it is not derived from the free surface.* That energy is set free in the form of heat in the process of adsorption is an established fact.

8. *The Primary Seat of Motion.*

If the weeping of volatile liquids were a surface phenomenon solely due to local differences of tension at the free surface, it would be independent of the nature of the vessel in which the reaction takes place. If, on the other hand, it is due, solely or mainly, to the interaction between the inner surface of the vessel and the adjacent layer of the liquid resulting in an interface-pressure, the nature of the vessel must be of paramount importance.

In order to make this crucial test the behaviour of weeping mixtures in divers kinds of vessels was studied, and it was found that *the reaction is completely absent in paraffin-coated vessels. Although paraffin is wetted by all volatile liquids, and is, therefore, a substance to which films and tears can adhere,* there is, neither at the moment of contact nor at any time afterwards, the slightest trace of peripheral expansion. Many volatile mixtures and solutions were tried, with the same negative result.

It may be thought that contamination of the free surface of the liquid by dissolved paraffin inhibits the reaction but, as already pointed out, every trace of reaction is absent from the very beginning, before the liquid has had the time to dissolve any of the paraffin. If any weeping liquid, such as alcohol or acetone, which dissolve paraffin only in traces, after proving inert during a short contact with the paraffin coating, is transferred to a clean clock-glass, the reaction commences immediately and runs its usual course. It is only in cases where the liquid has been given time to be converted into a saturated solution of paraffin that the reaction, after the liquid has been transferred to the glass vessel and after a normal beginning, gradually loses in intensity, and may even finally cease altogether. In such cases, however, it will be found that *the glass beneath the marginal film has become coated with a layer of paraffin* deposited from the liquid, and that it is not a contamination of the free surface, but of the solid interface, which inhibits the reaction.

9. *Substances which lower Surface Tension.*

It remains to be mentioned that the formation of tears is inhibited by the presence of those substances which are remarkable for the lowering effect they have on the free

surface-tension of water. A 10 per cent. alcoholic solution of soap is quite inert; saturated solutions of bile salts or saponin in alcohol react very sluggishly. The admixture of a small quantity of iso-amyl-alcohol to weeping mixtures brings the reaction quickly to an end. It seems, therefore, that these substances act not only at the free surface, but also at the liquid-solid interface.

In connexion herewith it is of interest to record the fact that if a glass beaker, wet on the inside, is inverted over any volatile liquid, the sheet of aqueous moisture at once separates into drops, leaving the rest of the inner surface dry, which means that the adhesion of the water to the glass is lowered in an even higher degree than its surface-tension; for whereas before the normal surface-tension of the water could not overcome its adhesion to the glass and contract the liquid sheet into drops, the lowered surface-tension is now able to do so.

Another pertinent observation of theoretical interest is the following. If a clock-glass is wetted by benzene or by iso-amyl-alcohol, the absorbed moisture adheres so firmly that it cannot be removed by shaking. But if a mixture containing one part of iso-amyl-alcohol and two to three of benzene is poured into a clock-glass, and the latter tilted in different directions, the mixture can be seen peeling off the glass, leaving the surface perfectly dry.

10. *Liquid-solid Interface Tension.*

An interface-pressure can result only from a "wet" contact between a liquid and a solid, and the foregoing experiments are intended to demonstrate the existence of such a pressure in volatile liquids. A "dry" contact, on the other hand, between a liquid and a solid, as, for instance, between mercury and glass or porcelain, produces interface-tension with a resulting convex meniscus.

The experiments were in part made in the Biochemical Department of the Liverpool University. It is my pleasant duty to thank Prof. W. Ramsden for most helpful criticisms, and to express to him and to Prof. I. S. Macdonald my grateful recognition of the facilities offered to me.

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XLI. *Theory of the Velocity of Diffusion of Strong Electrolytes in Dilute Solution.* *By* G. S. Hartley, *B.Sc.**

THE subject of diffusion velocity in liquid systems is one which, doubtless owing to the difficulty and inaccuracy of the experimental technique, has received in recent years only scant attention. Its principal application has been in biochemistry as a means of examining the size of colloidal micelles. The order of accuracy here required was not such as to instigate any inquiry into the theory beyond the classical treatment laid down by Nernst [1] and Einstein [2].

That the diffusion coefficient of electrolytes is dependent on the concentration and, in the case of strong electrolytes, generally passes through a minimum at a concentration of about normal or half-normal, has long been known. Oeholm attempted to coordinate this variation with the osmotic pressure and freezing-point "anomalies," but the freezing-point data from which he worked seem too scant to justify the very close agreement with theory that he found to hold good to nearly normal concentrations.

The agreement was, however, more significant than Oeholm himself seemed to realize. Although the theory of complete dissociation was not current at the time, he introduced no unknown factor for the mobility of the undissociated molecule. The experimental evidence that no such factor was necessary was therefore unused evidence in support of the modern point of view.

The object of this paper is to consider the diffusion velocity of strong electrolytes in the light of the activity function, and to indicate the importance of diffusion velocity measurements to the modern theory of strong electrolytes.

The General Theory and the Effect of Solvent Transfer.

The classical theory of diffusion velocity considered the solute contained in any elementary layer of liquid, normal to the concentration gradient, to be subject to a uniform pressure equal to the difference of the osmotic pressure at the two surfaces of the layer, since this is the pressure that would act on a piston of material permeable only to the solvent introduced in place of this elementary layer. In the case of electrolytes, additional forces act on the ions, due to the gradient of electrical potential.

* Communicated by Prof. F. G. Donnan, F.R.S.

Though this method of treatment seems very artificial, its validity has been abundantly confirmed within the limits of experimental error in the case of dilute solution. In this paper the artificial concept of a uniform driving force will still be employed, but its magnitude will be derived from consideration of the work done during the diffusion process. The two treatments lead to the same result in simple dilute solutions (and neither can be expected to be valid in concentrated ones), but the latter has the advantage of presenting a clearer picture of the process and is more convenient to handle from the point of view of the activity function. Moreover, it remains valid in the case of a solute of graded composition, which was considered by the present author [5] in another paper*, where the simple osmotic pressure theory definitely breaks down.

Consider a vertical cylinder, closed at one end and filled with a liquid solution of two components, A and B, having a constant temperature but a gradient (vertical) of composition. Let us confine our attention to a layer of height δh, so small that the composition gradient within it can be regarded as constant over a small period of time.

If a small amount, δQ mols of A diffuse across this layer, then, owing to the lower end of the cylinder being closed, an amount $\frac{\bar{V}_A}{\bar{V}_B}\delta Q$ mols of B must pass in the reverse direction, where $\bar{V}_A$, $\bar{V}_B$ are the partial molal volumes of the two components in c.c.

If we were to carry out these transfers by a reversible

* The function α used in the paper referred to and called there the activity, should, defined as it was by equation (14) of the preceding paper, not have been so-called. It is really the product of the van't Hoff coefficient and the concentration, and, if this be borne in mind, the treatment is valid. The activity proper, a, is connected with this function by

$$C\, d\ln a = d\alpha.$$

The argument of p. 13 is considerably simplified by employing the activity proper, since we have:

$$\text{osmotic pressure gradient} = RTC\frac{d\ln a}{dh};$$

$$\text{diffusion pressure gradient} = RTC\frac{d\ln(a/a_s)}{dh};$$

$$\text{difference} \ldots\ldots\ldots\ldots = RTC\frac{d\ln a^s}{dh}.$$

mechanism, the amount of work done by the system would be given by

$$-\delta Q \,.\, \delta \bar{F}_A + \frac{\bar{V}_A}{\bar{V}_B} \delta Q \,.\, \delta \bar{F}_B, \quad . \quad . \quad . \quad . \quad (1)$$

where $\delta \bar{F}_A$ and $\delta \bar{F}_B$ are the differences of partial molal free energy of the components between the two concentrations concerned.

The fundamental equation of partial molal quantities gives

$$\delta F_B = -\frac{N_A}{N_B} \,.\, \delta \bar{F}_A,$$

where N_A, N_B are the mol fractions of the components. Substituting this in (1), we have

$$\text{work done} = -\delta Q \,.\, \delta \bar{F}_A \left(1 + \frac{N_A \bar{V}_A}{N_B \bar{V}_B}\right). \quad . \quad . \quad (2)$$

For the special case of a dilute solution of M mols A in a litre of B, the third factor of (2) admits of simplification. Since the solution is dilute, we assume $\bar{V}_B$ equal to the molal volume of the pure solvent, whence the number of mols of B per litre $= \frac{1000}{\bar{V}_B}$, whence the mol ratio $\frac{N_A}{N_B} = \frac{M \bar{V}_B}{1000}$, so that (2) may be rewritten

$$\text{work done} = -\delta Q \,.\, \delta \bar{F}_A \,.\, (1 + M \,.\, \bar{V}_A \,.\, 10^{-3}). \quad . \quad (3)$$

The second term of the third factor will be so small with regard to 1 that it is immaterial whether the concentration is defined in mols per litre of solvent or of solution.

The fundamental assumption of this theory of diffusion is that, when the same transfer takes place by diffusion, the amount of work expressed by (3) can be regarded as expended by a uniform force acting on the solute molecules in overcoming the viscous resistance of the solution.

Since the distance through which the solute is transferred is the height of the layer, the force associated with the solute must be

$$-\delta Q \,.\, \frac{\delta \bar{F}_A}{\delta h} \,.\, (1 + M \bar{V}_A \,.\, 10^{-3}).$$

In the case of an infinitely thin layer, we may therefore write

$$\text{force per mol of A} = -(1 + M \,.\, \bar{V}_A \,.\, 10^{-3}) \,.\, \frac{d \bar{F}_A}{dh}.$$

If we define the mobility U as the mean velocity with respect to the solvent produced in the solute molecules by unit force per mol of them, then the rate of transfer of A in mols per unit cross-section (normal to the gradient) per second will be given by

$$-(1+\mathrm{M}\,.\,\bar{\mathrm{V}}_{\mathrm{A}}\,.\,10^{-3})\,.\,\mathrm{M}\,.\,10^{-3}\,.\frac{d\bar{\mathrm{F}}_{\mathrm{A}}}{dh}\,.\,\mathrm{U},$$

the additional 10^{-3} term appearing on account of the concentration being measured in mols per litre, whereas the unit of length in the other factors is the cm., and hence the appropriate unit of volume the c.c.

The above expression gives the rate of transfer of solute with respect to the solvent. The latter will have a small backward flow on account of displacement by the solute molecules, and the absolute rate of transfer of A will therefore be less. The molecules of solute will in general be "solvated," *i. e.*, will carry with them a certain number of attached solvent molecules. The total volume which moves with one mol of solute we will call the "molal transference volume" of the solute, and will write it W_{A} c.c. The molal transference volume and partial molal volume will in general be very different. In dilute solutions of certain electrolytes, for instance, the partial molal volume is negative, which can never be the case for the transference volume.

The volume moving forward per unit section per second will therefore be

$$-(1+\mathrm{M}\bar{\mathrm{V}}_{\mathrm{A}}\,.\,10^{-3})\mathrm{M}\,.\,\mathrm{U}\,.\,\mathrm{W}_{\mathrm{A}}\frac{d\bar{\mathrm{F}}_{\mathrm{A}}}{dh}10^{-3}\text{ c.c.},$$

and an equal volume of solvent must flow back. The mean velocity of solvent will therefore be

$$(1+\mathrm{M}\bar{\mathrm{V}}_{\mathrm{A}}\,.\,10^{-3})\mathrm{M}\,.\,\mathrm{U}\,.\,\mathrm{W}_{\mathrm{A}}\frac{d\bar{\mathrm{F}}_{\mathrm{A}}}{dh}10^{-3}\text{ cm./sec.},$$

but the mean velocity of solute relative to solvent is

$$-(1+\mathrm{M}\bar{\mathrm{V}}_{\mathrm{A}}\,.\,10^{-3})\frac{d\bar{\mathrm{F}}_{\mathrm{A}}}{dh}\,.\,\mathrm{U}\text{ cm./sec.}$$

Whence the mean absolute velocity of solute

$$=-(1+\mathrm{M}\bar{\mathrm{V}}^{\mathrm{A}}\,.\,10^{-3})\,.\,\frac{d\bar{\mathrm{F}}_{\mathrm{A}}}{dh}\,.\,\mathrm{U}(1-\mathrm{M}\mathrm{W}_{\mathrm{A}}\,.\,10^{-3})\text{ cm./sec.},$$

and the absolute rate of transfer in mols per cm.^{2} per sec. will be

$$-(1+M\bar{V}_A \,.\, 10^{-3})(1-MW_A 10^{-3})\; M \,.\, U \,.\frac{d\bar{F}_A}{dh}.\, 10^{-3} \qquad (5)$$

since the second terms in both brackets will be small with respect to 1, (5) may be re-written

$$-(1-M[W_A-V_A]10^{-3})M \,.\, U \,.\frac{d\bar{F}_A}{dh}10^{-3}. \quad . \quad (6)$$

Fick's equation defines the diffusion coefficient D, by equating the rate of transfer to

$$-D\frac{dM}{dh}10^{-3}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Strong Electrolyte Solutions.

In the case of electrolytes, we shall work throughout in equivalents instead of mols. The concentration in equivalents per litre will be denoted by C, the partial equivalent and equivalent transference volume of the whole electrolyte, expressed in litres to dispense with the numerical factor of the previous section, by ϕ and ω.

Let the electrolyte under consideration produce ν_+ cations of charge n_+ and ν_- anions of charge n_-, from which it follows that

$$\nu_+ n_+ = \nu_- n_-, \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and, in all, ν ions, whence

$$\frac{\nu_+}{\nu} = \frac{n_-}{n_+ + n_-} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Complete dissociation of the electrolyte will be assumed.

Let F_+ be the partial molal free energy of the cation and a_+ its activity defined by

$$\delta F_+ = RT\,\delta \ln a_+ \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and $n_+ a_+ \longrightarrow C$ as $C \longrightarrow 0$.

The free energy change associated with the transfer of one gm. equivalent of cation without solvent transfer

$$= \frac{-\delta F_+}{n_+}$$

by (10)

$$= -\frac{RT}{n_+}\delta \ln a_+$$

$$= -RT\,\delta \ln {a_+}^{1/n_+}.$$

The free energy change associated with one equivalent of electrolyte therefore

$$= -RT(\delta \ln {a_+}^{1/n_+} + \delta \ln {a_-}^{1/n_-}).$$

The corresponding change under diffusion conditions when solvent transfer is not neglected is, on analogy with (3),

$$= -RT(1+C\phi)\ (\delta \ln {a^{+1/n_+}} + \delta \ln {a_-}^{1/n_-}).$$

Since, in the diffusion of a single electrolyte, the ions must always be transferred in equivalent quantities, we may write for the free energy change associated with the transfer, under diffusion conditions, of one gm. equivalent of ion,

$$-RT(1+C\phi)\delta \ln {a_+}^{1/n_+}$$

$$-RT(1+C\phi)\delta \ln {a_-}^{1/n_-}.$$

The forces per gm. ion, by which the statistical effect of the concentration gradient may be considered replaced, are therefore

$$-RT(1+C\phi)\frac{d \ln {a_+}^{1/n_+}}{dh}$$

and

$$-RT(1+C\phi)\frac{d \ln {a_-}^{1/n_-}}{dh}.$$

When R is expressed in ergs these forces will be in dynes. In addition there will act electrical forces of $F\frac{dE}{dh}10^7$ dynes per gm. equivalent, $+ve$ for the anion and $-ve$ for the cation where $\frac{dE}{dh}$ is the potential gradient in volts/cm., and F the equivalent of electricity in coulombs.

We shall first, in order to develop a generally valid equation, attribute to the ions different mobilities under the influence of "statistical" and electrical forces, namely, U_s and U_e for the cation and V_s and V_e for the anion, the units being cm./sec. per dyne/gm. equivalent.

The rates of transfer of the two ions in gm. equivalents per cm.^{2} per sec. with respect to the solvent, are

$$-\left[\mathrm{RT}(1+\mathrm{C}\phi)\frac{d\ln a_+^{1/n_+}}{dh}\mathrm{U}_s+\mathrm{F}\frac{d\mathrm{E}}{dh}10^7\,\mathrm{U}_e\right]\mathrm{C}\,.\,10^{-3}$$

and

$$-\left[\mathrm{RT}(1+\mathrm{C}\phi)\frac{d\ln a_-^{1/n_-}}{dh}\mathrm{V}_s-\mathrm{F}\frac{d\mathrm{E}}{dh}10^7\,\mathrm{V}_e\right]\mathrm{C}\,.\,10^{-3},$$

and therefore, on analogy with (5), the absolute equivalent rates of transfer, which, since they must be equal, we will call X, are

$$\mathrm{X}=-\mathrm{C}\,.\,10^{-3}(1-\mathrm{C}\omega)\left[\mathrm{RT}(1+\mathrm{C}\phi)\frac{d\ln a_+^{1/n_+}}{dh}\mathrm{U}_s+\mathrm{F}\frac{d\mathrm{E}}{dh}10^7\,\mathrm{U}_e\right]$$

$$\mathrm{X}=-\mathrm{C}\,10^{-3}(1-\mathrm{C}\omega)\left[\mathrm{RT}(1+\mathrm{C}\phi)\frac{d\ln a_-^{1/n_-}}{dh}\mathrm{V}_s-\mathrm{F}\frac{d\mathrm{E}}{dh}10^7\,\mathrm{V}_e\right].$$

Eliminating $\mathrm{F}\frac{d\mathrm{E}}{dh}$ we have

$$\mathrm{X}=-\mathrm{C}\,.\,10^{-3}(1-\mathrm{C}\omega)(1+\mathrm{C}\phi)\,\mathrm{RT}\frac{1}{\mathrm{U}_e+\mathrm{V}_e}\left[\mathrm{U}_s\mathrm{V}_e\frac{d\ln a_+^{1/n_+}}{dh}+\mathrm{U}_e\mathrm{V}_s\frac{d\ln a_-^{1/n_-}}{dh}\right].$$

Since, in dilute solution, $\mathrm{C}\phi$ and $\mathrm{C}\omega$ are small compared to 1, we may write

$$\mathrm{X}=-(1-\mathrm{C}\overline{\omega-\phi})\,\mathrm{RTC}\,10^{-3}\frac{1}{\mathrm{U}_e+\mathrm{V}_e}\left[\mathrm{U}_s\mathrm{V}_e\frac{d\ln a_+^{1/n_+}}{dh}+\mathrm{U}_e\mathrm{V}_s\frac{d\ln a_-^{1/n_-}}{dh}\right].$$

Combining this with the appropriate form of Fick's equation, $\mathrm{X}=-\mathrm{D}_c\frac{dc}{dh}10^{-3}$, we eliminate h and obtain

$$\mathrm{D}_c=(1-\mathrm{C}\overline{\omega-\phi})\,\mathrm{RT}\frac{1}{\mathrm{U}_e+\mathrm{V}_e}\left[\mathrm{U}_s\mathrm{V}_e\frac{d\ln a_+^{1/n_+}}{d\ln \mathrm{C}}+\mathrm{U}_e\mathrm{V}_s\frac{d\ln a_-^{1/n_-}}{d\ln \mathrm{C}}\right]. \quad (11)$$

At infinite dilution,

$$\mathrm{U}_s=\mathrm{U}_e=\mathrm{U},\qquad \mathrm{V}_s=\mathrm{V}_e=\mathrm{V},\quad \text{and}\quad \frac{d\ln a}{d\ln \mathrm{C}}=1,$$

whence

$$\mathrm{D}_0=\mathrm{RT}\frac{\mathrm{UV}}{\mathrm{U}+\mathrm{V}}\left(\frac{1}{n_+}+\frac{1}{n_-}\right), \quad . \quad . \quad . \quad (12)$$

which is the equation first quoted by Haskell [15] and attributed by him to A. A. Noyes and which reduces to the well-known Nernst formula

$$D_0 = 2RT\frac{UV}{U+V},$$

for uni-univalent electrolytes.

If we accept the complete dissociation theory, we must assume a very marked decrease of mobility with increasing concentration to explain the decrease of equivalent conductance.

If we assume the ions to move with the mobility derived from conductance measurements, irrespectively of the nature or directions of the forces acting, we must write in equation (11),

$$U_s = U_e = \frac{u_c}{F^2}\cdot 10^{-7},$$

where u_c is the equivalent conductance of the cation at the concentration concerned. A similar relationship will hold for the anion, whence we have

$$D_c = (1+C\overline{\omega-\phi})\frac{RT}{F^2}\,10^{-7}\,\frac{u_c v_c}{u_c+v_c}\,\frac{d\ln a_+^{1/n_+}a_-^{1/n_-}}{d\ln C}.$$

By introducing equation (9) and defining, with Lewis, the mean activity

$$a_{\pm} = (a_+^{\nu_+}\cdot a_-^{\nu_-})^{1/\nu},$$

this becomes

$$D_c = (1+C\overline{\omega-\phi})\frac{RT}{F^2}\cdot 10^{-7}\frac{u_c v_c}{u_c+v_c}\left(\frac{1}{n_+}+\frac{1}{n_-}\right)\frac{d\ln a_{\pm}}{d\ln C}. \quad (13)$$

In terms of equivalent conductance, (12) is

$$D_0 = \frac{RT}{F^2}\cdot 10^{-7}\frac{u_0 v_0}{u_0-v_0}\left(\frac{1}{n_+}+\frac{1}{n_-}\right). \quad (12\,A)$$

Whence, combining with (13), we have, as the equation of variation of the diffusion constant, on this first assumption with regard to mobility,

$$D_c = D_0(1+C\overline{\omega-\phi})\frac{u_c v_c}{u_c+v_c}\cdot\frac{u_0+v_0}{u_0 v_0}\frac{d\ln a_{\pm}}{d\ln C}. \quad (13\,A)$$

The experimental evidence collected in the last section of this paper shows that this equation is quite inapplicable, and the assumption with regard to mobility therefore invalid.

For purposes of calculation, it has therefore been simplified by the assumption, tantamount to neglecting variation of transport number with concentration that

$$\frac{u_c}{u_0} = \frac{v_c}{v_0} = \frac{\lambda_c}{\lambda_0},$$

where λ is the equivalent conductance of the electrolyte. The approximate equation is

$$D_c = D_0(1 + C\overline{\omega - \phi})\frac{\lambda_c}{\lambda_0}\frac{d \ln a_{\pm}}{d \ln C}. \quad . \quad . \quad (13\,B)$$

Of the theories put forward to account for the considerable decrease of equivalent conductance, while retaining the theory of complete ionization, the earlier ones, of which that of Ghosh is the best known, postulated a loose association between cations and anions. Any associated pair, while retaining most of the degrees of freedom of two separate ions, is not, owing to the total charge being zero, during the associated life, influenced by an electric field. This factor in reducing apparent mobility will clearly not apply to the "statistical" force which acts on both ions in the same direction. On a theory of this type we should expect U_e and U_e to be different, U_e being equal to $\frac{u_c}{F^2}.10^{-7}$ and U_s differing from $\frac{u_0}{F^2}.10^{-7}$ only in so far as the viscosity of the solution effects the mobility.

The relationship of mobility and viscosity has been the subject of much discussion and research [4], and no satisfactory conclusion has been arrived at. The difficulty has always been to eliminate the effect of other significant factors, such as solvation of the solute molecules or ions, which are nearly always changed simultaneously with the viscosity. The relationship is certainly an inverse one and not very far from simple inverse proportionality. McInnes [11] proposes the empirical equation

$$\text{mobility} \times \text{viscosity}^{0{\cdot}7} = \text{constant}$$

for ions of strong electrolytes, basing the equation on the mobilities of the Cl^- ion in solution of hydrogen and alkaline chlorides of equal concentration.

Since the viscosity correction for solutions below decinormal concentration is very small, McInnes' empirical formula will be assumed for the purpose of this paper, it being clearly understood that this is only a provisional

assumption. Since, if the ion size could increase without limit, accordance with Stokes' equation must be approached, it is clearly untenable to assume that the exponent of viscosity in the McInnes type of equation can be the same for all ions.

On the Ghosh theory, accepting McInnes' equation, we should have

$$U_s = \frac{u_0}{F^2} \cdot 10^{-7} \eta_c^{-0\cdot7},$$

where η_c is the viscosity of the solution with reference to pure solvent as standard.

On these assumptions, equation (11) becomes

$$D_c = (1 + C\overline{\omega - \phi}) \frac{RT}{F^2} \cdot 10^{-7} \eta_c^{-0\cdot7} \frac{1}{u_c + v_c} \left[u_0 v_c \frac{d \ln a_+^{1/n_+}}{d \ln C} + v_0 u_c \frac{d \ln a_-^{1/n_-}}{d \ln C} \right]$$

$$= (1 + C\overline{\omega - \phi}) \frac{RT}{F^2} \cdot 10^{-7} \eta_c^{-0\cdot7} \frac{u_0 v_0}{u_c + v_c} \cdot \frac{u_0 + v_0}{u_c + v_c} \left[\frac{v_c}{v_0} \cdot \frac{d \ln a_+^{1/n_+}}{d \ln C} + \frac{u_c}{u_0} \cdot \frac{d \ln a_-^{1/n_-}}{d \ln C} \right]$$

$$= (1 + C\overline{\omega - \phi}) \frac{RT}{F^2} \cdot 10^{-7} \eta_c^{-0\cdot7} \frac{u_0 v_0}{u_0 + v_0} \left[\frac{t_c^-}{t_0^-} \cdot \frac{d \ln a_+^{1/n_+}}{d \ln C} + \frac{t_c^+}{t_0^+} \cdot \frac{d \ln a_-^{1/n_-}}{d \ln C} \right], \quad (14\text{B})$$

where t^+ is the transport number of the cation. Since we are concerned with mobility in respect to the solvent, the transport numbers employed must be the true transport numbers of Buchböck and Washburn.

Introducing equation (9) and the mean activity, equation (14 B) reduces to

$$D_c = -(1 + C\overline{\omega - \phi}) \frac{RT}{F^2} 10^{-7} \eta_c^{-0\cdot7} \frac{u_0 v_0}{u_0 + v_0} \left[\frac{1}{n_+} + \frac{1}{n_-} \right] \left[\frac{d \ln a^{\pm}}{d \ln C} + \frac{t_c^- - t_0^-}{\nu} \left(\frac{\nu_+}{t_0^-} \frac{d \ln a_+}{d \ln C} - \frac{\nu_-}{t_0^+} \frac{d \ln a_-}{d \ln C} \right) \right], \quad (14)$$

dividing by equation (12 A), we obtain as the equation of variation,

$$D_c = D_0 (1 + C\overline{\omega - \phi}) \eta_c^{-0\cdot7} \left[\frac{d \ln a^{\pm}}{d \ln C} + \frac{t_c^- - t_0^-}{\nu} \left[\frac{\nu_+}{t_0^-} \frac{d \ln a_+}{d \ln C} - \frac{\nu_-}{t_0^+} \frac{d \ln a_-}{d \ln C} \right] \right]. \quad (14\text{A})$$

The most successful of the strong electrolyte theories, that of Debye and Hückel, attributes the decrease of equivalent conductance to a quite different cause from that envisaged by Ghosh. On this theory an ion is regarded as surrounded by an "atmosphere" of equal and opposite charge, whose radius is a function of the concentration. If the central charge be imagined instantaneously annihilated, there is an appreciable time lag in the destruction of the atmosphere. Under the influence of an electric field, the central ion and its atmosphere are drawn in opposite directions, and, as a result of the time lag, the ion moves with a distorted atmosphere of which it is no longer the centre. The effect of this can be shown to be that of an increased viscous drag on the moving ion. This factor no longer operates in the case of simple diffusion, since the ions of opposite kinds necessarily move at the same speed in the same direction.

On the basis of the Debye-Hückel theory and the McInnes viscosity rule, we have, therefore,

$$U_e = U_s = \frac{u_0}{F^2} 10^{-7} \eta_c^{-0\cdot7}.$$

On this theory, therefore, equation (11) becomes

$$D_c = (1 + C\overline{\omega - \phi}) \frac{RT}{F^2} 10^{-7} \eta_c^{-0\cdot7} \frac{u_0 v_0}{u_0 + v_0} \frac{d \ln a^{\pm}}{d \ln C}, \quad (15)$$

and combining with equation (12 A),

$$D_c = D_0 (1 + C\overline{\omega - \phi}) \eta_c^{-0\cdot7} \frac{d \ln a^{\pm}}{d \ln C} \quad . \quad . \quad . \quad (15\,A)$$

of the equations (13), (14), and (15), only (14) involves the individual ion activities, and that only to a second order extent, since the transport numbers vary by only a small fraction of their value between concentrations below decinormal.

The Experimental Evidence.

The more doubtful assumptions made in the theoretical treatment of the preceding sections become insignificant in infinitely dilute solution. In this limiting case only the fundamental assumption of the theory—namely, that the solute can be regarded as subject to a uniform force which, in acting against the viscous resistance of the solvent, dissipates energy during diffusion equal to the change in free energy of the system—remains questionable. It seems

probable, therefore, that equation (12 A) will be definitely invalid or absolutely exact. The experimental evidence [5] shows that the equation predicts values approximately true at concentrations in which diffusion can be measured and that the values tend to the theoretical Nernst values at infinite dilution. Equation (12 A) will therefore be considered exact.

Equations (13 A), (14 A), and (15 A) will give values for the ratio of the diffusion coefficient at a finite concentration to that at infinite dilution. We could test their validity, therefore, by comparing the ratios so obtained with the ratios of the experimental values at the chosen concentration to the theoretical values of equation (12 A). Since the error in diffusion velocity measurements increases with decreasing concentration, it is advisable to choose as high a concentration as is consistent with the assumption of complete dissociation. Accordingly data were collected for several electrolytes at decinormal concentrations.

The values of the diffusion coefficient in cm.^{2}/day in decinormal solutions were taken from the figures of Oeholm [5], Clack [6], and Thovert [7], intrapolated where necessary, and corrected to 18° C. by means of the temperature coefficients given in Oeholm's paper. The diffusion coefficients at infinite dilution were worked out for 18° C., accepting the latest values for the equivalent conductance at infinite dilution given by Landolt and Börnstein.

Values of $\frac{d \ln a^{\pm}}{d \ln C}$ were calculated from the figures given by Lewis and Randall in their text-book on 'Thermodynamics', and when possible also from later work of the American authors [8]. In order to calculate this term, use was made of the relationship

$$\frac{d \ln a^{\pm}}{d \ln C} = 1 + \frac{d \ln \gamma}{d \ln C},$$

where γ is the activity coefficient.

The term $(\omega - \phi)$ is one which cannot be exactly evaluated in the present state of our knowledge. It was assumed that it could be identified with the volume of the water sheath of one gm. equivalent of electrolyte, and therefore given by ·018 W, where W is the sum of the number of H_2O molecules attached to each $+ve$ and $-ve$ charge. The values of W were taken from the compilation of Remy [9], or the values of Riesenfeld and Reinhold [10], reduced to those of Remy, where they referred to the same ion and proportionally in

other cases. The correction introduced by this factor is in any case small, being greatest for NaCl, where it amounts to less than 2 per cent.

Values for η_c were taken where possible from the paper of McInnes [11].

The transport number term of equation (14 A) was the one that could be evaluated with least certainty. Values of

TABLE.

Where more than one value for a quantity is given, the mean value was employed in the calculations. The numbers in brackets refer to the text references in columns 4, 5, and 6, and to equations in 7.

Salt and D_0.	$\eta_{0\cdot1}$ and W	$\frac{\lambda_{0\cdot1}}{\lambda_0}$.	$t_{0\cdot1}^- - t_0^-$.	$\frac{d \ln a\pm}{d \ln C}$.	$D_{0\cdot1}/D_0$ observed.	$D_{0\cdot1}/D_0$ theoretical.
HCl	1·005	0·939	−0·011 (11)	0·932 (14)	0·918 (5)	0·878 (13)
2·431	4	—	−0·010 (12)	0·948 (8A)	0·889 (7)	0·906 (14)
			−0·017 (9)	0·944 (8B)	—	0·930 (15)
KCl	0·998	0·861	0·000	0·916 (14)	0·952 (5)	0·776 (13)
1·460	7	—	—	0·913 (8C)	0·960 (7)	0·907 (14)
				0·911 (8B)	0·892 (6)	0·907 (15)
NaCl	1·009	0·844	+0·012 (11)	0·918 (14)	0·951 (5)	0·756 (13)
1·173	10	—	—	0·909 (8B)	0·861 (7)	0·888 (14)
					0·912 (6)	0·893 (15)
KOH	?	0·937	+0·020 (12)	0·919 (14)	0·880 (5)	0·863 (13)
2·109	5	—	—	0·929 (8B)	—	0·896 (14)
				0·943 (8D)	—	0·920 (15)
KNO_3	0·997	0·829	−0·008 (12)	0·816 (14)	0·887 (7)	0·676 (13)
1·420	8	—	—	—	0·870 (6)	0·805 (14)
						0·806 (15)
H_2SO_4	1·010	0·609	−0·008 (13)	0·679 (14)	0·69 (7)	0·414 (13)
1·890	4	—	—	0 684 (8E)	—	0·653 (14)
						0·673 (15)
K_2SO_4	?	0·715	0·000 (13)	0·759 (14)	0·77 (7)	0·544 (13)
1·119	7	—	—	—	—	0·748 (14)
						0·748 (15)

$t_c^- - t_0^-$ were taken from McInnes [11], Kohlrausch [12], Remy [9], or the compilation of Noyes and Falk [13], some of the values being intrapolated in the light of the more detailed ones. Provisional values for the individual ion activities were taken from Lewis and Randall's [14] textbook.

These data are assembled in the table. It is clear from them that the least reliable of all the measurements concerned, in view of their importance, are those of the diffusion velocity itself. At present no decision can be

made on experimental evidence between equations (14 A) and (15 A), but in the case of HCl the difference between the values for the ratio predicted by these equations is considerable. Comparing HCl and KCl, the evidence seems to be more favourable to the former equation. It is evident that (13 A) predicts far too low values for the ratio, which is additional evidence that the mobility of the ions is not independent of the nature and direction of the driving force.

On the theory of incomplete dissociation, the effective driving force on the solute must be considered only to a small extent to decrease with increasing concentration. The marked decrease in diffusion velocity must then have been explained by the introduction of a factor for the mobility of the undissociated molecule. This mobility must therefore have been less than the harmonic mean of the ion mobilities, an assumption for which there is no evidence. The approximate agreement of the experimental evidence with the predictions of equations (14) and (15) is therefore an argument in favour of the complete dissociation theory.

The form of the diffusion coefficient-concentration curves predicted by equations (14 A) and (15 A) is, in dilute solution, similar to that of the function $\frac{d \ln a^{\pm}}{d \ln C}$. The gradient of this function is half that of the activity coefficient at zero concentration, and its minimum value is greater than that of the latter and is reached at a lower concentration, the value attaining unity again at the minimum of the activity coefficient. The effect of the other terms is to flatten out the diffusion coefficient curve at higher concentrations, since $(1-C\overline{\omega-\phi})$ is the most important of them and decreases with increasing concentration. The equations therefore predict a diffusion coefficient decreasing rapidly with increasing concentration in very dilute solution, specially rapidly for multivalent electrolytes, passing through a flat minimum at about normal or half normal and increasing slowly beyond. This is quite in accord with experimental evidence, but an exact comparison would not, in the present state of the latter, be instructive, even if the method and assumptions of the theory could be considered applicable in the more concentrated solutions.

Incompletely Dissociated Electrolytes.

Haskell[15] made an attempt to account for the decrease of diffusion velocity with increasing concentration on the assumption of incomplete dissociation. His conclusions with

regard to the mobility of the undissociated molecule are probably quite erroneous because he ignored the effect of interionic forces on the "free" ions, which, in 1908, was not appreciated as it is to-day. Since the present paper was written, however, two further attempts in this direction have been published, in which it is very surprising to find the effect of these forces still ignored. In other respects Haskell's treatment of the subject seems to the present author to be more exact than that of the more recent papers. McBain and Liu[16] propose an equation which, for uni-univalent salts, becomes

$$D = \frac{iRT}{\frac{\alpha}{U} + \frac{\alpha}{V} + \frac{1-\alpha}{M}},$$

where α is the degree of dissociation, i the van't Hoff factor, and M the mobility of the undissociated molecule. McBain, Rysellberge, and Squance[17] employ a similar equation for a unibivalent salt. The equation is derived by analogy from the Nernst equation, which may be written

$$D = \frac{2RT}{\frac{1}{U} + \frac{1}{V}}.$$

Whereas Haskell considered the ionized and unionized salt as diffusing independently, the McBain equation implies a very different assumption, for, in the Nernst equation, the mobility terms are added in a reciprocal form in the denominator rather than directly in the numerator, because the condition of electrical neutrality demands that the ions diffuse at equivalent rates. That the McBain equation involves an error seems to the present author to be made clear if the case of a hypothetical salt whose undissociated molecule is immobile is considered. Clearly this immobility will not restrain the diffusion of the ions, but the McBain equation gives a value of $D=0$ for $M=0$.

The equation for the case of an incompletely dissociated salt derived by Haskell's method, with introduction of activity considerations as in the foregoing theory, is, if we ignore the viscosity and displacement terms and also the possible existence of intermediate ions,

$$D = RT \cdot \frac{d \ln a_{\pm}}{d \ln C} \cdot \left(\frac{1}{n_+} + \frac{1}{n_-}\right) \cdot \left[\alpha \cdot \frac{UV}{U+V} + (1-\alpha)M\right]. \quad (16)$$

where M is measured in cm./sec. per dyne/gm. equivalent.

Since we should expect, on the basis of Stokes' law, that M will be greater than $\frac{UV}{U+V}$, equation (16) predicts a higher value of D for the case of an incompletely dissociated electrolyte than it would have were the decrease of activity coefficient due solely to the forces on the "free" ions.

In conclusion, the author would like to express his indebtedness to Prof. F. G. Donnan for valuable criticism during the preparation of this paper.

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XLII. *A simple Experiment for Investigating and Demonstrating the Peltier-effect.* By Dr. U. Ph. Lely *.

TWO rods of copper (ϕ=7 mm., length 10 cm.) are soldered to an iron rod of equal dimensions. If a galvanometer is connected to the ends of this rod and if the

* Communicated by the Author.

rod is heated asymmetrically a current will flow through the galvanometer ; the direction of the current depends on the asymmetry, the intensity on the degree of this asymmetry.

Now we disconnect the galvanometer from the rod and connect it to a source of direct current, and send through the rod a current of some 15 amp. After one or two minutes we disconnect the source of direct current and connect the rod immediately to the galvanometer. The galvanometer shows a current which gradually diminishes in intensity. The switching over may be effected by a suitable switch.

The heat developed in the rod because of its resistance, according to Joule, has no influence, for this heat causes a symmetrical temperature distribution along the rod ; but the Peltier-effect has a result. One junction is heated, the other is cooled ; the temperature distribution is asymmetrical and results, after the switching over, into a current in the galvanometer. Inverting the direction of the direct current causes a galvanometer current in the opposite direction.

Alternating current will have no result if the symmetry is good. If the symmetry is not quite good it may be improved by connecting the galvanometer to movable or sliding contacts on the copper parts of the rod.

The effect may be increased by soldering together a number of alternate pieces of iron and copper, the ending parts being copper. The Peltier-effects at all junctions will cooperate, the heat produced according to Joule will be eliminated, as it produces no asymmetry. The initial galvanometer current is proportional to the number of junctions.

At the junctions the Peltier-effects heat or cool the rod ; the heat is conducted from the hotter junctions towards the colder ones. The thermal time-constant of this phenomenon is equal to that shown by the decreasing deflexion of the galvanometer after its insertion into the circuit.

The thermal resistance is proportional to the length of the rod, the capacity of heat also. Thus the time-constant is proportional to the square of the length of the elements.

The asymmetry of heating, caused by the Peltier-effect, has a limiting value for a given current, proportional to the length of the element of the rod ; the initial galvanometer current is proportional to this length if the heating current has been sent long enough through the rod (some 15 minutes). If only during short intervals, say some 30 seconds, a current is sent through the rod, the initial galvanometer current is proportional to the time during which the rod carried current.

The stronger the rod the lesser the cooling or heating influence of the surrounding air and of radiation. For exact investigations strong rods are recommended.

The Peltier-effect may be investigated easily by this method, which is applicable for liquids also. The results will be more reliable than when operating with the older methods. For demonstrations in the lecture-room it is a most easy method, as it never fails. For students it will be a useful educational experiment.

The Hague, Christelijk Gymnasium, Holland.
May 1931.

XLIII. *Experiments on Cylinders oscillating in a Stream of Water.* *By* A. Thom, *D.Sc., Ph.D., A.R.T.C., Carnegie Teaching Fellow, University of Glasgow* *.

A CYLINDER suspended transversely in a moving fluid can be made to oscillate continuously if the natural frequency of the suspended cylinder is the same as that of the eddies which are known to be given off by a cylinder at nearly all values of Reynolds's Number. This phenomenon provides a method of measuring the frequency of these eddies and of estimating the strength of the impulse given to the cylinder. Many experimenters have measured the frequency at normal values of Reynolds's Number. The present paper deals with measurements carried down to the lowest value of Reynolds's Number at which eddies exist. It is shown that the impulse decreases with decreasing speed until it becomes zero at the Reynolds's Number, where eddying stops. No claim to accuracy is made for these experiments, as the conditions do not permit of refined measurements. Probably the best method of producing these eddies is that where a cylinder is moved through still water. This method could not have been used for the experiments described here even had the apparatus been available.

The channel used has a working section of about 5 in. × 5 in., and was designed primarily for experiments with oil. The distribution of velocity at the working section is not good, and when water is being used there is probably eddying in the stream itself as it approaches the cylinder. To improve the conditions a honeycomb and perforated plates were

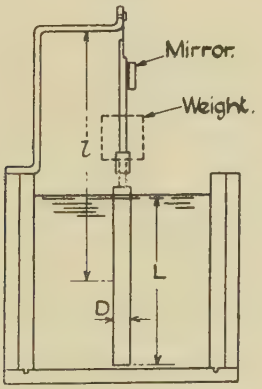
* Communicated by the Author.

fitted upstream, the perforations being enlarged locally and tested repeatedly to make the flow as uniform as possible; but even after many efforts unavoidable unsteadiness and non-uniformity remained, and this must be borne in mind when interpreting the results.

The arrangement of the cylinder in the channel was as shown in fig. 1. The cylinder hung as a pendulum on a light spring, free to swing across the stream. The height of the point of suspension, the weight, and the spring could all be changed. Let θ=the semiamplitude of the swing, f=frequency, and l, L, and D be as in fig. 1. Then, for an angular semiamplitude θ the cross velocity of the mid-point of the cylinder is given by

$$v = 2\pi f l\theta \cos 2\pi ft. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Fig. 1.



The assumption is made that the whole submerged portion (length L, diameter D) moves with this speed. Let U be the undisturbed speed of the fluid and q the resultant velocity of the cylinder relative to the fluid. Assume that the total fluid force can be written

$$F = K_D \rho DLq^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The component of this acting across the channel is Fv/q or $K_D \rho DLqv$. It will be seen later that v is always considerably less than U, so that a reasonable approximation for present purposes is to put $q = U$, giving for the cross force

$$K_D \rho DLUv. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

By dimensional considerations the maximum value of the cross force given by each eddy should be of the form

$$f(\mathrm{R})\rho \mathrm{DLU}^2,$$

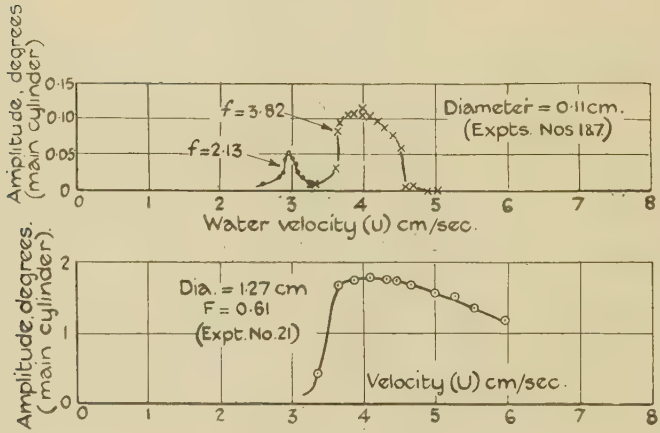
where R is Reynolds's Number. If the cross force is simple harmonic it can be written

$$\mathrm{K_E}\rho \mathrm{DLU}^2 \cos 2\pi ft,$$

where $\mathrm{K_E}$ $(=f(\mathrm{R}))$ is a coefficient giving the eddy force. Equating these values leads to

$$\frac{\mathrm{K_E}}{\mathrm{K_D}} = \frac{2\pi fl\theta}{\mathrm{U}} \text{ or } \frac{v_m}{\mathrm{U}}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Fig. 2.

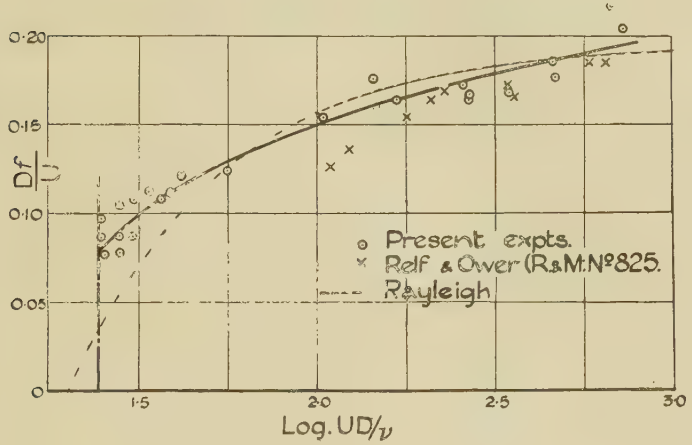


Typical amplitude curves.

where $v_m(=2\pi fl\theta)$ is the maximum value of v. The first experiments were directed towards evaluating the coefficients $\mathrm{K_E}$ and $\mathrm{D}f/\mathrm{U}$. Five different cylinders were used of diameters from 0·055 in. to 0·5 in. The period of each could be varied by applying different weights and springs. The procedure in each experiment was as follows :—Having chosen a suitable combination of weight and spring the water was brought to a definite speed and the conditions allowed to settle. The amplitude of the swing developed was then measured by noting the movement of a spot of light thrown across the room on to a screen by the mirror on the pendulum. This measurement was repeated for a number of water speeds. Typical curves so obtained are shown in fig. 2. Generally the rise in amplitude was more

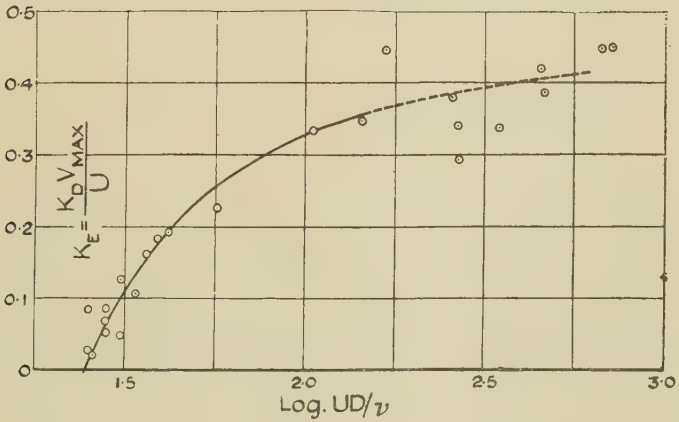
rapid than the fall, possibly due to the slower moving water at the bottom of the channel becoming operative at a higher speed. The damping introduced in the case of the larger cylinders by the close proximity of the channel floor is also

Fig. 3.



Frequency and strength of eddies.

Fig. 4.



operative and cannot be allowed for. The maximum amplitude and the velocity at which it occurred were thus found. These quantities are given in the accompanying table (p. 494), together with the coefficients found from them. These coefficients are shown plotted in figs. 3 and 4. It will be seen

No.	Observed. D. cm.	U. cm./sec.	f. 1/sec.	θ. degrees.	l. cm.	Assumed. K_D.	Results. $\frac{UD}{\gamma}$.	$\frac{Df}{U}$.	K_R.
1	0·11	3·0	2·13	0·055	17	0·95	28	0·078	0·068
2	0·11	2·7	2·16	0·042	25	0·98	25	0·087	0·087
3	0·11	3·0	2·37	0·067	17	0·95	28	0·087	0·087
4	0·11	3·3	2·61	0·069	17	0·87	31	0·087	0·127
5	0·11	2·9	2·65	0·017	17	0·98	25	0·098	0·028
6	0·11	3·0	2·86	0·021	25	0·95	28	0·105	0·051
7	0·11	3·9	3·82	0·11	17	0·82	36	0·108	0 162
8	0·11	3·6	3·65	0·046	25	0·84	34	0·112	0·108
9	0 14	2·6	2·0	0·040	17	0·87	31	0·108	0·049
10	0·14	3·3	2·63	0·153	17	0·81	39	0·111	0·184
11	0·14	3·5	3·03	0·212	12	0·80	42	0·121	0·192
12	0·14	4·7	4·2	0·185	17	0·74	56	0·125	0·228
13	0·318	3·9	1·89	0·55	17	0·68	105	0·154	0·33
14	0·318	5·3	2·94	0·71	12	0·67	143	0·176	0·35
15	0·318	6·2	3·18	0·71	17	0·66	167	0·163	0·45
16	0·636	5·0	1·296	0·75	25	0·64	270	0·165	0·34
17	0·636	4·8	1·30	0·80	25	0·64	258	0·172	0·38
18	0·636	5·0	1·31	0·63	25	0·61	270	0·167	0·29
19	0·636	6·5	1·71	1·13	17	0·61	350	0·168	0·34
20	0·636	6·9	2·18	—	17	—	372	0·200	—
21	1·27	4·2	0·61	1·78	25	0·59	452	0·185	0·42
22	1·27	4·3	0·60	1·74	25	0·58	464	0·177	0·39
23	1·27	6·2	1·07	1·72	25	0·55	677	0·219	0·45
24	1·27	6·7	1·08	1·88	25	0·64	727	0·204	0·45
25									

In the above table θ is the maximum amplitude of the cylinder and U is the speed at which it occurs.

from fig. 4 that the impulse becomes zero when $R=24$ or $\log_{10}R=1{\cdot}38$. As far as could be ascertained the ratio Df/U (fig. 3) does not reach zero. Several attempts were made to extend this curve downwards by using slightly lower frequencies than those shown in experiments nos. 1 and 2, but without success. If synchronism took place the amplitude was too small to be detected. It is, of course, possible that the effect was masked by the unsteady flow causing the very weak eddies to be irregular, but, on the other hand, K_E obtained from the same experiments has been traced almost to zero, so that it appears possible that Df/U never becomes smaller than 0·075. The author's experiments on the pressures round cylinders at low Reynolds's Numbers * bear out the conclusion that some fundamental change takes place at or about $R=30$, as in this neighbourhood there seems to be a sharp bend in the pressure curves for individual positions on the rear surface of the cylinder.

At the higher values of Reynolds's Number K_E has a value of 0·3 to 0·4, so that by (4) the maximum velocity of the cylinder is about half the stream velocity, K_D averaging about 0·7.

The measurements of Relf and Ower † on the frequency of the eddies were carried down to Reynolds's Number 110. So far as these experiments overlap the agreement is almost within the scattering of the points, as will be seen from fig. 3.

An empirical relation between Df/U and R was suggested in 1915 by Rayleigh ‡, namely,

$$Df/U = 0{\cdot}195\,(1-\ 20{\cdot}1/R).$$

This expression is shown on fig. 3 by a dotted curve. In view of the fact that it is unlikely that the formula was intended for extrapolation to low velocities, the agreement with the present experiments is remarkable.

In order to measure approximately the strength and epoch of the eddies the following apparatus was used :—A small cylinder (about 1 mm. diameter) was mounted behind and parallel to the main cylinder ($\frac{1}{2}$ in. diameter) so as to be free to swing (*a*) only across the channel or (*b*) only longitudinally. The period of this cylinder, which shall be called

* Advisory Committee for Aeronautics, R. & M. No. 1194, fig. 7.

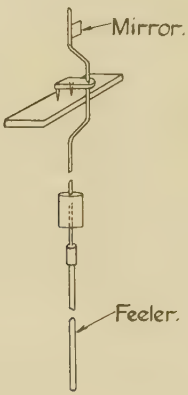
† "The Singing of Circular and Streamline Wires," R. & M. No. 825.

‡ Phil. Mag. xxix. p. 435. See also Richardson, Proc. Phys. Soc. xxxvi. pp. 153–165.

hereafter the "feeler" (fig. 5), was adjusted to have the same value as that of the main cylinder, and both were arranged to throw spots of light on a screen so that these moved up and down side by side. The motion of the main cylinder was damped by a piece of gauze attached to it in such a manner that the gauze moved to and fro in a separate vessel. The gauze was submerged to such an extent that the motion of the cylinder while being considerably reduced was still sufficient to permit a suitable movement of the spot of light.

The water speed was brought to 4·1 ft. per second, which is practically the speed at which the cylinder had its maximum amplitude when free. Then the feeler (arranged to be

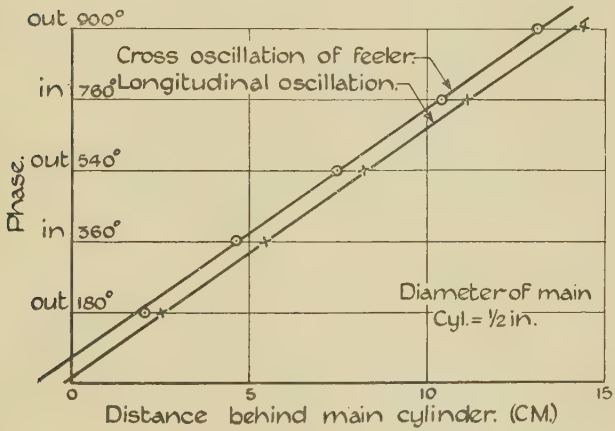
Fig. 5.



free to move across the stream) was moved by a series of short steps along a line parallel to the flow, but about 1·3 cm. from the centre line of the channel, until a position was found where the two spots, and so the two cylinders, were in phase. Several such positions were found, the distance between consecutive positions being the distance between the eddies on one side of the Kármán street. The intermediate positions where the spots were out of phase were also found. The results are shown in fig. 6, from which it will be seen that the distance (a) between successive eddies is about 5·7 cm. Experiments made at different distances from the centre line showed that within the limits of the accuracy with which the positions of phase agreement could be located these lay on straight lines across the channel. It will be shown that theoretically this result might be expected.

The feeler was now set to be free to oscillate along the channel, and the above experiment repeated. The results shown in fig. 6 were obtained along the left side of the stream about 2 cm. from the centre (in order to make certain of being outside the Kármán street). The feeler and the cylinder are considered to be in phase when the former swings downstream at the same time as the latter swings to the left (facing downstream). Again the distance between the eddies is about 5·7 cm. (see fig. 6). Since the frequency was 0·61 per sec., the speed of the eddies relative to the cylinder was $0{\cdot}61 \times 5{\cdot}7 = 3{\cdot}5$ cm./sec. The speed of the eddies relative to the water (ω) is the difference between

Fig. 6.



Position of phase agreement for feeler and main cylinder.

this speed, 3·5 cm./sec., and the water speed, 4·1 cm./sec., or about 0·6 cm./sec. If the eddies form a true Kármán street, then the vortex strength is given by *

$$K = \omega a \sqrt{8}.$$

The above values give

$$K = 9{\cdot}5 \text{ cm.}^2/\text{sec.},$$

so that the coefficient K/aU is 0·42, a result which agrees well with von Kármán's experimental results †. It should

* Lamb, 'Hydrodynamics,' 5th ed. p. 156.
† Lock, R. & M. No. 980.

be noted, however, that the above value depends on the difference of two velocities neither of which is known accurately, so that too great reliance should not be placed on the result. To find the relation between the position of the eddies and the position of the main cylinder from fig. 6 it is necessary to find how the eddies are placed when the feeler has, say, its maximum velocity. This matter has been investigated by considering the effect of a Kármán street on a small body free to oscillate across the stream with a period equal to that of the eddies. Take the x-axis parallel to the stream and downstream, and the y-axis to the left. If the component of the water velocity across the channel is small and periodic, and consists only of the first harmonic terms, then considerations similar to those already given show that the feeler settles down to such a condition that it will at each instant have the same velocity as the cross component of the water. It will, in fact, follow the latter, so that there is never any cross force on it. Actually the expression for the cross velocity of the water cannot be represented by a simple first harmonic, but it is proposed to assume that if v is expressed as a Fourier series it will be sufficient to retain the first harmonic terms only.

Consider first a single row of vortices. The y component is given by *

$$v = \frac{K}{2a} \frac{\sin(2\pi x/a)}{\cosh(2\pi y/a) - \cos(2\pi x/a)},$$

the origin being at a vortex. Assuming then that v can be written

$$v = A\cos(2\pi x/a) + B\sin(2\pi x/a),$$

the coefficients are given by

$$\pi A = \frac{K}{2a} \int_{-\pi}^{+\pi} \frac{\sin\gamma\cos\gamma\, d\gamma}{\cosh(2\pi y/a) - \cos\gamma}$$

and

$$\pi B = \frac{K}{2a} \int_{-\pi}^{+\pi} \frac{\sin^2\gamma\, d\gamma}{\cosh(2\pi y/a) - \cos\gamma},$$

where $\gamma = 2\pi x/a$. These are reduced to standard integrals by writing, for instance, the second as

$$\pi B = \frac{K}{2a} \int_{-\pi}^{+\pi} \left\{ \cos\gamma + \cosh(2\pi y/a) - \frac{\sinh^2(2\pi y/a)}{\cosh(2\pi y/a) - \cos\gamma} \right\} d\gamma.$$

* Lamb, *loc. cit.*

On integration these coefficients are found to be

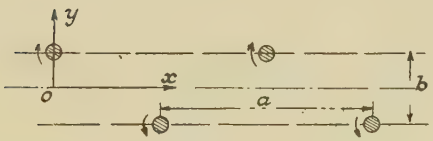
$$A = 0, \quad B = \frac{K}{a}\{\cosh(2\pi y/a) \pm \sinh(2\pi y/a)\}, \quad . \quad (5)$$

where the negative sign is appropriate to positive values of y and the positive sign to negative values.

Now consider the Kármán street shown in fig. 7. The upper row of vortices are negative and lie on the line $y = b/2$. The lower lines are positive and lie on the line $y = -b/2$. Considering the region above the upper row the contribution of the vortices in this row to the cross velocity is, by (5),

$$v_1 = -\frac{K}{a}\left\{\cosh\frac{2\pi}{a}\left(y-\frac{b}{2}\right) - \sinh\frac{2\pi}{a}\left(y-\frac{b}{2}\right)\right\}\sin\frac{2\pi x}{a},$$

Fig. 7.



and the contribution of the lower is

$$v_2 = \frac{K}{a}\left\{\cosh\frac{2\pi}{a}\left(y+\frac{b}{2}\right) - \sinh\frac{2\pi}{a}\left(y+\frac{b}{2}\right)\right\}\sin\frac{2\pi}{a}\left(x-\frac{a}{2}\right).$$

Adding and reducing leads to

$$v = v_1 + v_2 = -\frac{2K}{a}\cosh\frac{\pi b}{a}\left\{\cosh\frac{2\pi y}{a} - \sin\frac{2\pi y}{a}\right\}\sin\gamma.$$

Treating the central region in the same way gives

$$v = -\frac{2K}{a}\cosh\frac{2\pi y}{a}\left\{\cosh\frac{\pi b}{a} - \sinh\frac{\pi b}{a}\right\}\sin\gamma.$$

For a Kármán street we have the simplification

$$\cosh^2\left(\frac{\pi b}{a}\right) = 2\,;$$

so the final form is

$$v = A_1\cos\gamma + B_1\sin\gamma,$$

where

$$A_1 = 0,$$

$$B_1 = -2\sqrt{2}\frac{K}{a}\left(\cosh\frac{2\pi y}{a} - \sinh\frac{2\pi y}{a}\right) \text{ outside the rows,}$$

$$B_1 = -2\frac{K}{a}(\sqrt{2}-1)\cosh\frac{2\pi y}{a} \text{ between the rows.}$$

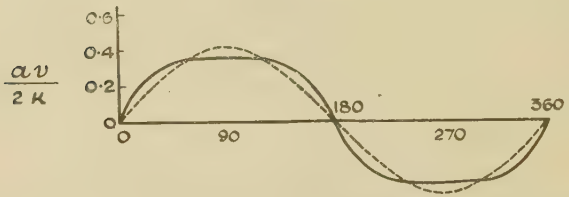
Treating the longitudinal velocity component U in the same manner yields

$$A_2 = -2\sqrt{2}\frac{K}{a}\left(\sinh\frac{2\pi y}{a} - \cosh\frac{2\pi y}{a}\right) \text{ outside the rows,}$$

$$A_2 = -2\frac{K}{a}(\sqrt{2}-1)\sinh\frac{2\pi y}{a} \text{ between the rows,}$$

$$B_2 = 0.$$

Fig. 8.



Actual values of v (the cross velocity) along the centre line of the Kármán street, compared with the first harmonic of the Fourier expansion.

In fig. 8 a comparison is given of the actual calculated cross velocity along the centre line of the Kármán street with the first harmonic, showing that in this region at least the agreement is reasonable. Close to the eddies the agreement is naturally not good.

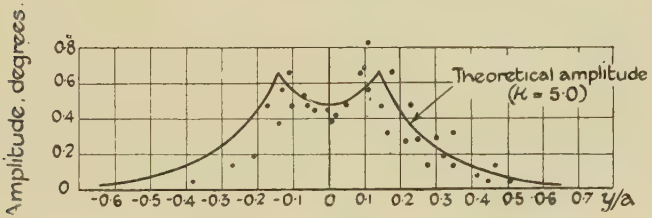
It will be noticed that the above expressions for the velocity place the node of each velocity curve at the same value of x. It has already been remarked that the phase of the feeler is constant for positions in line across the channel. This agreement is in itself some support for the above procedure. To obtain a further comparison the amplitude of the motion of the feeler was measured for two cases:

1. With the feeler free to oscillate across the channel the amplitude was measured at a number of points along a line across the channel 7·9 cm. behind the cylinder.

2. With the feeler free to oscillate parallel to the flow the amplitude was measured at points on a line across the channel 5·0 cm. behind the cylinder.

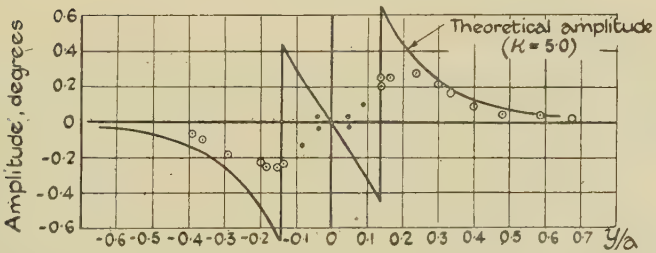
The results are shown in figs. 9 and 10. In case 2 when the feeler was in phase with the cylinder the amplitude was considered positive, and when out of phase negative. Near the centre the results were uncertain, being sometimes in phase and sometimes out of phase. If ∂ is the semiamplitude of the feeler, and l_1 the length from the point of

Fig. 9.



Amplitude of feeler oscillating across channel 7·9 cm. behind cylinder (diam. of cylinder = 1·27 cm.).

Fig. 10.



Amplitude of feeler oscillating along channel 5·1 cm. behind cylinder.

suspension to the centre M of the submerged portion, then the maximum velocity of M is given by $2\pi\, l_1\partial$. Equating this to the maximum velocity of the water, as given by the coefficient of the first harmonic, we obtain for :

1. Transverse oscillations,

$$\theta = B_1 \div 2\pi f l_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

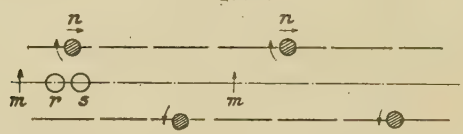
2. Cross oscillations,

$$\theta = A_2 \div 2\pi f l_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

In these experiments $l_1 = 22{\cdot}3$ cm., $a = 5{\cdot}7$ cm., $f = 0{\cdot}61$. Taking $K = 5{\cdot}0$, the lines shown full on figs. 9 and 10 were plotted from (6) and (7). As the value of K obtained previously was 9·7, the amplitude of the feeler is about half what the above theory indicates. This is, perhaps, not surprising when the irregular nature of the eddies is considered. The distance between the rows indicated on fig. 9 appears to be in agreement with the theoretical value for the Kármán street, namely $0{\cdot}28\,a$.

While the theory given above may not predict the amplitude, it probably places the node in the right position. Assuming this to be so, it is possible from the above experiments to find the relation between the position of the eddy and the position of the main cylinder in its swing. In other words, we can find the position of the cylinder relative to the Kármán street when the force on the former is a maximum. Thus from the theory $m\,m$ are the positions in the street (fig. 11) of maximum cross velocity, and this occurs

Fig. 11.



when the feeler is in the middle of its swing. From fig. 6 the main cylinder is 4·7 cm. (or 300°) upstream from the feeler in the same phase as itself, and so is at r (fig. 11) when central.

Again, from the theory the positions of maximum downstream velocity on the left side are at $n\,n$, and from fig. 6 the main cylinder is 5·5 cm. (347°) upstream from the eddy in the same phase as itself, and so is at s (fig. 11) when central. Thus the two methods differ by only 0·6 cm., and the mean of the two places an eddy position just passing the cylinder when the latter is central and moving towards the eddy. But the central position in a forced and damped oscillation is the position of maximum force. Thus the cylinder experiences the greatest force to the right (left) when an eddy on the right (left) is just forming.

If this force is merely due to the presence of the eddy then we should expect that there would be an increment to the drag as well as a "lift" produced, but attempts to get the cylinder to oscillate longitudinally failed. That a wire only oscillates across the current has been noted by other

observers. The conclusion is that the side force is due to a circulation about the cylinder of the same sign as the eddy being formed. Hence either (*a*) the eddy itself has caused a circulation about the cylinder or (*b*) the eddy on the other side of the street has, by withdrawing itself from the neighbourhood of the cylinder, left a circulation of opposite sign behind it. With either explanation each eddy must produce enough circulation to annul that left by its predecessor and then build up that required for the force.

It is interesting to estimate the value of the side force which would be produced on the cylinder if each eddy produced a circulation about the cylinder equal to its own strength. This side force would be $K\rho LV$. Equating this to the expression used previously for the maximum side force, namely, $K_E\rho DLU^2$ gives $K_E=\frac{K}{DU}$. In the present experiment this makes $K_E=1{\cdot}9$. Reynolds's Number for the experiment is about 470, and a reference to fig. 4 shows that the actual value of K_E would be about 0·38, so that apparently the circulation actually built up round the cylinder does not exceed one-quarter of the strength of each eddy. Presumably this would be the case if each eddy contributed a circulation equal to half its own strength, since half of the contribution would be absorbed in annulling the existing circulation.

The above work forms part of a research programme being carried out in the James Watt Engineering Laboratories, University of Glasgow, under the directorship of Prof. J. D. Cormack.

December 1930.

XLIV. *The Law of Photo-elastic Extinction.* *By* J. Kuno, *Assistant Professor of Civil Engineering, Kyushu Imperial University, Fukuoka* *.

[Plates X.–XII.]

I. *Introduction*

SINCE the time of Sir David Brewster, experiments have been made showing that if the incident ray falls perpendicularly upon the plane of a transparent elastic plate strained

* Communicated by the Author.

two-dimensionally by a system of loads, the light is broken up into two components, one polarized in the direction of a principal axis and the other in the direction of another axis. Examining a specimen between crossed nicols, we find that the light passing through a point at which the principal axes coincide in direction with the principal planes of the nicols is extinguished. This darkness, referring to the directions of the principal axes, we shall speak of as the photo-elastic extinction of the first kind. Points of simultaneous extinction generally form a curve called an isoclinic line.

Each of the component rays broken up in the specimen changes its velocity of transmission according to the magnitude of the stress which acts in the vibration direction of that ray. Accordingly, complete transmission through the specimen produces a certain amount of phase-difference between the two.

If a specimen is placed in the beam of circularly polarized monochromatic light between the crossed nicols, the intensity of light I passing through the analyser may be represented by an equation $I = A^2 \sin^2 \frac{1}{2}\delta$, where A is a constant depending on the nature of the light used and δ is the phase-difference between the two components *. Now consider a point giving such a phase-difference as $\delta = 2n\pi$ where n is an integer; then we have $I = 0$, that is, the light is extinguished and the field becomes dark at the point. This darkness, referring to the magnitude of the stress, we shall speak of as the photo-elastic extinction of the second kind, which occurs periodically as δ increases. Thus n represents the order of extinction.

II. *Reduction of the Law.*

The quantitative relation between the stress and its optical effect has been generally represented by either of the equations

$$\left.\begin{aligned} r &= CSd, \\ \delta &= 2\pi CSd/\lambda, \end{aligned}\right\} \quad \cdots\cdots \quad (1)$$

where r is the relative retardation corresponding to δ, λ is the wave-length of the light used, S is the principal stress difference, d is the thickness of the specimen, and C is the photo-elastic (stress-optical) coefficient. The coefficient C was expressed by Prof. Filon in a unit called a "brewster" (Proc. Roy. Soc. A, lxxxiii. p. 576, 1910), while it has been

* 'Technology Report of the Kyushu Imp. University,' v. p. 164 (1930).

scarcely employed in the engineering application of photo-elasticity because of the practical difficulties of measuring the retardation in angströms. Now, putting

$$\delta = 2\pi \mathrm{S}d/\mathrm{K}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

we get

$$\mathrm{S}d = \mathrm{K}n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{I.})$$

at the point of the photo-elastic extinction of the second kind.

Thus, at the point of such extinction, the principal stress-difference multiplied by the thickness of the specimen is proportional to the order of extinction. This fact we shall refer to as the Law of Photo-elastic Extinction, and the constant K as the Coefficient of Photo-elastic Extinction. In a specimen of uniform thickness, the law may be expressed in another form, namely,

$$\mathrm{S} = kn, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{II.})$$

where $k = \mathrm{K}/d$. Hence the principal stress-difference is directly proportional to the order of extinction.

Measuring S in kg./cm.^{2} and d in cm., K is expressed in kg./cm. and k in kg./cm.^{2} Comparing (1) with (2), we have $\mathrm{CK} = \lambda$. Expressing C in brewsters, K in kg./cm., and λ in angströms, we have a numerical relation for transforming K into C and *vice versa*, namely, $\mathrm{CK} = \lambda/9{\cdot}8$.

III. *Load-extinction Curve.*

Let a Babinet's quartz-wedge compensator be inserted between crossed nicols, so that the principal planes of vibration of the former may be inclined at 45° to the principal planes of the latter. The distance through which a wedge is moved in order to replace a dark band with an adjoining one under the cross-hairs we shall denote by a. Moving the wedge the distance a changes the phase-difference by 2π. In the compensator employed by the writer, a was found equal to 3·82 mm. for the monochromatic light of 5461 angströms.

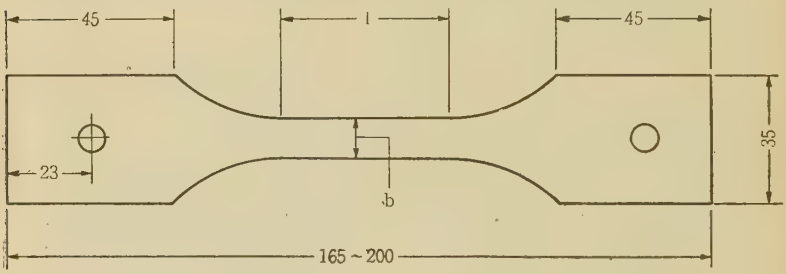
Next, inserting a tension or compression specimen of uniform section between the compensator and the polarizer arranged as before, so that the directions of principal axes may coincide with the principal planes of the compensator, we find the central band shifted to another point. Pl. X. shows the general view of the apparatus. The quartz wedge is now to be moved by the micrometer-screw until the central band is again bisected by the cross-hairs. If this distance,

the extinction displacement, is denoted by x, we have $\delta = 2\pi x/a$. Then we obtain from this and the equation (2)

$$P = xKb/a, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where b is the width of the specimen and P is the axial load applied to the specimen.

If the stress-optical behaviour of the specimen arranged as above is studied by increasing the load gradually, measuring the extinction displacement at intervals, and plotting a curve with the loads as ordinates and the corresponding extinction displacements as abscissæ, we have a load-extinction curve. Since the tangent of the slope of a load-extinction curve indicates the value of Kb/a in the equation (3), the coefficient K is equal to the tangent value multiplied by a constant a/b so far as the curve is straight.



$l = 35, 70.$
$b = 10 \sim 15.$
$d = 4 \sim 10.$

Unit in mm.

IV. *The Primitive Value of the Coefficient* K.

Eleven tension specimens, as shown in the above figure, were first prepared in order to determine the coefficient K for phenolite, manufactured by the Institute of Physical and Chemical Research, Tokyo (Scientific Papers I.P.C.R. vii. p. 79, 1927). The day before each testing, the specimen was annealed by heating it at 65° C. for about an hour in a thermostat and allowing it to cool off very slowly, the object being the removal of initial stresses. A cement-briquette testing-machine of Michaelis's type was used as the straining apparatus. The grips of the machine were modified to fit into the holes pierced at the two ends of the specimens to enable the pull to be applied. Pl. XI. shows the tension device, in which the transparent specimen is photographed black as ebonite because phenolite is yellowish light brown in colour and absorbs the light sensitive to the photographic

plate. For light, the green line of the mercury-vapour lamp was used throughout the experiments.

It was attempted first to obtain the load-extinction curves by increasing the load by ΔP kg. at intervals of Δt minutes, and measuring the extinction displacements at the instant of one minute after each increase of the load, five series of tests being carried out by changing the load and time increments. The load-extinction curves proved linear, the value of K being found in kg./cm. as follows :—

ΔP	30	15	5	5	5
Δt	2	2	2	5	10
K.....	10·9	10·3	9·9	9·6	8·9

These results indicate that the method of testing employed above fails to give a constant value of K.

The second attempt was performed by giving less than 5 seconds to carry out the three operations of loading, reading the scale and unloading for a definite value of the load, and repeating such an observation at intervals of more than 5 minutes with the same specimen, the load being varied within the limits of 10 and 80 kg. All the load-extinction curves of eleven specimens were found linear. Determined by the method of least squares, the coefficient K varied from 10·75 to 11·44 kg./cm., showing that it seemed to be little affected by changing the load increments. The mean value of K was 11·0 kg./cm.

For the purpose of compression tests, a steel frame was inserted between the grips of the testing-machine to convert the original tension into a compressive force, the device being shown in Pl. XII. In order to examine the same materials that were used in the previous tests, nine specimens were prepared by cutting off both ends of the tension specimens and reducing their length to 72 mm. Each specimen was tested by the instantaneous method, as employed in the tension test, the load limits being 30 and 100 kg. Determined by the method of least squares, the value of K varied from 10·66 to 11·53 kg./cm., giving the mean value of 11·0 kg./cm.

The value of the coefficient of photo-elastic extinction determined by the instantaneous method as employed in the above tests we shall refer to as the primitive value of K, and denote it by K_0.

V. *The General Value of the Coefficient* K.

The equation (3) can be transformed into $Sad = xK$, the left- and right-hand members of which must respectively be

constant so long as the load remains constant, while x may undergo a change in consequence of the optical creep. Hence K may be a function of time to neutralize the time effect upon x.

The stress-optical condition at the instant of being loaded will now be denoted by $Sad = x_0 K_0$, and the condition just t minutes after being loaded by $Sad = (x_0 + X)K_t$ Eliminating x_0 from these two relations, we have

$$K_t = K_0(1 + K_0 Y/S)^{-1}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $Y = X/ad$, representing the optical creep per unit thickness expressed in the compensator period.

Eleven tension specimens of phenolite were examined under various loads ($10 \sim 230$ kg./cm.^{2}), each test being performed by keeping the load constant and reading X at intervals of 1 minute for the first 20 minutes and then at intervals of 10 minutes for the following 100 minutes. On calculating Y and plotting it to time on the logarithmic paper, we found that the creep-time relation could be represented by equations of the form $Y = pt^r$. The results of more than sixty tests showed that p was proportional to S, and we had

$$\left.\begin{aligned} Y &= \tfrac{1}{300} S t^{0.36} \quad (t < 15 \text{ min.}), \\ Y &= \tfrac{1}{250} S t^{0.29} \quad (15 \text{ min.} < t < 120 \text{ min.}) \end{aligned}\right\} \quad . \quad . \quad (5)$$

Inserting (5) into (4), we get

$$K_t = K_0(1 + mK_0 t^r)^{-1}, \quad . \quad . \quad . \quad . \quad (\text{III.})$$

where m represents the numerical coefficients and r the indices in (5). Taking K_0 at 11·0 kg./cm., we have

$$K_1 = 10{\cdot}6, \quad K_2 = 10{\cdot}5, \quad K_5 = 10{\cdot}3,$$
$$K_{15} = 10{\cdot}0, \quad K_{30} = 9{\cdot}8, \quad K_{120} = 9{\cdot}4.$$

Accordingly it is obvious that the optical creep should not be neglected in both cases of tracing the isochromatic lines and of determining the stress-optical constant. This fact may also be true in celluloid and bakelite, because the optical creep in them is comparatively large (Phil. Trans. A, ccxxiii. p. 89 ; Proc. Phys. Math. Soc. Japan, ser. 3, vii. p. 160).

VI. *Comparison of Phenolite with Glass, Celluloid, and Bakelite from the Stress-optical point of view.*

1. Just in the same way as for phenolite, the values of K_0 for some other materials were obtained as follows :—

	Materials.		
	Glass.	Celluloid.	Bakelite.
K_θ in. kg./cm.	234·4	48·8	12·7
C in. brewster	2·4	11·4	43·9

Three specimens made of so-called Belgian polished glass were tested. Celluloid specimens, twelve in all, were cut from the sheets manufactured by the Dainihon Celluloid Co., Japan, the Du Pont Viscoloid Co., U.S.A., and the British Xylonite Co., London. Three bakelite specimens were prepared out of the pure bakelite of C state manufactured by the Sankyo Co., Tokyo.

In regard to the optical sensibility, the above results show that glass compares very unfavourably with other material.

2. Phenolite has considerable initial stresses in it, but they can be removed by one hour's annealing at 65° C. On the other hand, initial stresses in bakelite are so marked and stubborn that they cannot easily be removed as in phenolite. In this point bakelite compares unfavourably with phenolite.

3. The value of stress corresponding to the end of linearity in the load-extinction curve we shall speak of as the optically proportional limit, and denote it by S_0. A number of tests for phenolite showed that it was equal to about 280 kg./cm.^{2} for tension and 300 kg./cm.^{2} for compression. The law of photo-elastic extinction holds true only within S_0. Hence there is the allowable maximum limit in the orders of extinction, and we shall refer to it as the extinction limit. Denoting it by n_0, we have

$$n_0 = S_0 d / K_0. \quad . \quad . \quad . \quad . \quad . \quad \text{(IV.)}$$

Taking S_0 as 250 kg./cm.^{2} for celluloid (Phil. Trans. A, ccxxi. p. 161) and as 280 for phenolite, we get

d in cm.	1·0	0·6	0·4
n_0 for phenolite	25·4	15·3	10·2
n_0 for celluloid	5·1	3·1	2·1

Thus the stress-optical ability of celluloid is nearly one-fifth of that of phenolite.

4. Other elastic constants expressed in the kg.–cm. system were approximately as follows:—

	Materials.		
	Phenolite.	Bakelite.	Celluloid.
Ultimate tensile strength	430	250	430
Ultimate compressive strength.....	1600	1100	1200
Yield-point (compression)	1600	1000	540
Young's modulus, 10^4	3·6	3·7	2·7

VII. *The Extinction Method of Photo-elasticity, the Optical Creep being taken into account.*

In the engineering application of photo-elasticity the optical effect observed must be remarkably affected by the time that has elapsed since the load was put on, which tends to give a result of misjudging the value of stress. As a way out of this trouble, the extinction method of photo-elasticity is recommended, the details being as follows:—.

1. To record the simultaneous states of extinction, the specimen placed in the beam of circularly polarized monochromatic light should be photographed at the instant that just t minutes will have exactly elapsed after being loaded.

2. To make the order of extinction clear, further photographs, if necessary, should be taken at various stages of the load between zero and the final amount. Kinematographing is preferable, if the apparatus is at hand.

3. To discriminate the sign of the principal stress difference, a few points on the specimen should qualitatively be examined with the ordinary comparison test piece, the material and the thickness of which need not be necessarily the same as those of the specimen.

4. The isoclinic lines should then be recorded.

5. The coefficient K_t should be determined for the same material as that of the specimen, from which k_t should be calculated.

6. The values of the principal stress differences for the black fringes photographed should be estimated by the law $S=nk_t$. The principal stresses themselves should be determined by the method of graphical integration.

VIII *Summary.*

1. The law of photo-elastic extinction has been defined and experimentally justified, showing that the principal stress difference multiplied by the thickness of the specimen is proportional to the order of extinction.

2. The primitive value of the coefficient K is 11·0 kg./cm. in average for phenolite. The value of K varies with the time that has elapsed from the instant of loading to that of observing.

3. The extinction method of photo-elasticity eliminates the time effect upon the specimen.

4. Phenolite seems to be preferable to glass, celluloid, and bakelite as the specimens for the photo-elastic observations.

XLV. *The Thermal Expansion and Atomic Heat of Solid Mercury.* *By* L. G. Carpenter, *B.A., B.Sc., and* F. H. Oakley, *B.Sc., University College, Southampton* *.

Introduction.

THE atomic heat of solid mercury at constant pressure has recently been determined † over the temperature range from 200° A. to the melting point (234°·2 A.). In order to deduce from the experimental results the atomic heat at constant volume, which is the theoretically more interesting quantity, it is necessary to know the compressibility, atomic volume, and coefficient of thermal expansion. At the time when the atomic heat measurements were made, however, it appeared from the literature that the thermal expansion was extremely uncertain, and so a special determination was necessary. This has now been carried out, and the results obtained, together with the resulting values for the atomic heat at constant volume, form the subject matter of the present paper.

The unreliability and inconsistency of the hitherto published data on the cubical expansion coefficient of solid mercury is rather surprising. The only available values

* Communicated by the Authors.

† L. G. Carpenter and L. G. Stoodley, Phil. Mag. x. p. 249 (1930). This paper will subsequently be referred to as C. & S.

seem to be that of Dewar *, who obtained $8{\cdot}87 \times 10^{-5}$ from $-188{\cdot}7^{\circ}$ C. to the melting-point, of Grunmach †, who obtained $12{\cdot}3 \times 10^{-5}$ from -80° C. to the melting-point, and of Bridgman ‡, who made two determinations just below the melting-point and obtained 12·5 and $16{\cdot}5 \times 10^{-5}$. That the two values of Bridgman are discordant is not surprising, since they were admittedly very rough and obtained quite incidentally in the course of an investigation on the change of volume on freezing.

For solid mercury near its melting-point the difference $C_p - C_v$ between the two atomic heats is of the order of half a calorie, and, as is well-known, this difference depends on the square of the expansion coefficient. As the atomic heats themselves are of the order of 6 calories it is evident that an error of 3 per cent. in the value of the expansion coefficient will produce an error of about $\frac{1}{2}$ per cent. in the value of C_v deduced from the experimentally determined C_p. As in the atomic heat experiments C_p itself was considered to be certain only to within somewhat less than 1 per cent., it appeared that a precision of about 3 per cent. would be sufficient in the determinations of the expansion coefficient. The data recorded in this paper were therefore obtained to this order of accuracy.

Experimental Arrangements and Procedure.

The solid mercury, whose expansion was to be measured, nearly filled a pyrex dilatometer which had a long vertical capillary stem. The space not occupied by mercury was filled with pure ethyl alcohol to a convenient height in the capillary. Thus the expansion of the mercury on heating caused a rise of the alcohol meniscus in the capillary, and hence, after making correction for the effect of the alcohol, the expansion of the mercury could be deduced.

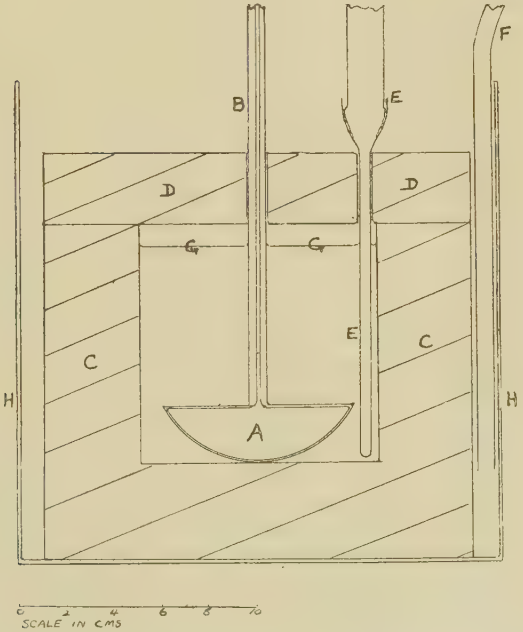
The arrangement of the apparatus is shown in fig. 1. A is the bulb of the dilatometer of capacity about 75 c.c., B its capillary stem, whose internal diameter was about 1 mm., and E is a platinum resistance thermometer which measured the temperature of A. In order to ensure uniformity of temperature the dilatometer bulb and platinum thermometer were enclosed in an aluminium casting CC in the form of a cylinder with a coaxial cylindrical cavity. The open end of the casting was closed by a thick aluminium

* Proc. Roy. Soc. lxx. p. 237 (1902).
† *Phys. Zeits.* iii. p. 133 (1902).
‡ Am. Acad. Sci. Proc. xlvii. p. 343 (1911).

lid D, which for convenience was made in two halves and bored to admit the passage of the dilatometer stem B and the platinum thermometer E.

The aluminium casting, which weighed about 10 kilograms, stood in a large tin HH, of such dimensions that an annular space of about 1 cm. was left between the casting and the tin. The tube F served to pump liquid air into this space when it was desired to cool the casting and the enclosed dilatometer.

Fig. 1.



The whole apparatus was supported inside a large wooden box and packed round with cotton wool, so that there was in every direction a thickness of at least 20 cm. of cotton wool between the surface of the casting and the air of the room. The thermal insulation was such that when the room temperature was about 20° C. and the aluminium casting at about −80° C. the rate of temperature rise of the casting was 5° C. per hour. It was calculated that, under these conditions, the maximum temperature difference which existed between different parts of the casting could not exceed 1/20° C.

The upper part of the capillary protruded through the cotton wool for about 10 cm. into free air and terminated in a cup which had been sealed on at the top to facilitate filling. The inner cylindrical cavity in the aluminium was filled with methylated spirit to the level GG in order to ensure that the dilatometer bulb and the coil of the platinum thermometer, which was on the same level as the bulb, were at the same temperature. In the determination of the expansion coefficient the cooled casting was allowed to heat up slowly under the action of the heat leaking in through the cotton wool from the room outside. The height of the alcohol meniscus was observed by means of a cathetometer, and the resistance of the platinum thermometer measured with a Callendar-Griffiths bridge, both types of observation being recorded as functions of time. In order that the expansion of the mercury might be correctly deduced from the movement of the alcohol meniscus in the capillary tube it was obviously of the greatest importance that the solid mercury in the bulb should be surrounded on all sides by alcohol and that there should be no empty spaces between the mercury and the pyrex. Two distinct methods of filling were therefore tried. In one of these about a cubic centimetre of alcohol was first introduced into the bulb, and the bulb then immersed in a Dewar flask of methylated spirit at about $-60°$ C. Some liquid mercury was then run into the dilatometer and froze on touching the bottom of the bulb. More mercury was added, a little at a time, until it filled the whole bulb to within 1 or 2 cubic centimetres. The remainder of the space, including the capillary, was then filled with alcohol, and the dilatometer transferred from the Dewar flask to the aluminium casting, which had previously been cooled below $-40°$ C. When the dilatometer had been filled in this way we were careful to satisfy ourselves that there was a continuous layer of alcohol between the solid mercury and the glass walls of the bulb.

In the second method of filling a small quantity of alcohol was first swilled round in the bulb in order to form a film on the surface of the pyrex. The bulb was then nearly filled with liquid mercury and placed in the Dewar flask of cooled methylated spirit. When the mercury originally in the bulb had frozen more mercury was added to fill the space caused by contraction on freezing. The dilatometer was then quickly taken out of the Dewar flask and inverted. The lump of solid mercury was found to fall away from the pyrex mould in which it had been cast and to shake about loosely in the bulb. In order to allow of

this test and yet restrict the volume of alcohol necessary to occupy the "dead space" in the bulb the latter was made in the form of a cap of a sphere, as shown in fig. 1. Finally, alcohol was added to fill up "dead space," as in the first method of filling. In this second method also we were satisfied that the solid mercury was surrounded on all sides by alcohol ; further, we found no systematic differences between the values of expansion coefficient obtained when the dilatometer had been filled in these two different ways.

The actual experimental procedure was as follows :—The dilatometer was filled in one of the ways mentioned above and transferred to the aluminium casting, which had previously been cooled by liquid air. The platinum thermometer was then placed in position, the lid D put on, and the cotton wool lagging arranged so that the casting was well insulated from the room. More liquid air was pumped in through F, and in evaporating cooled down the aluminium to some 10° C. below the temperature at which it was intended to start readings. The apparatus was then allowed to heat up naturally under the influence of heat from the room, and after about two hours the alcohol meniscus reappeared in the capillary tube above the top of the cotton wool. This long time interval between cooling with liquid air and starting to take observations was necessary in order that the dilatometer bulb and aluminium casting might attain the same temperature and rise steadily at the same rate.

When the alcohol meniscus appeared above the cotton wool lagging, readings of its height and of the resistance of the platinum thermometer were taken about every minute until the meniscus had traversed the 10 cm. of capillary that was in free air and overflowed into the cup at the top. The temperature of the air in the neighbourhood of the capillary stem was read by a mercury-in-glass thermometer. These observations provided the data for the calculation of the expansion of mercury at the mean temperature of the dilatometer during the time which the alcohol meniscus took to traverse the 10 cm. of capillary.

In order to make another determination at a higher temperature, the temperature rise of the apparatus was allowed to continue until the platinum thermometer indicated a temperature a little below the mean temperature at which the next determination was desired, the alcohol in the 10 cm. of capillary sucked out by means of a fine glass squirt, and the above procedure repeated. In this way a series of determinations of the expansion coefficient

could be made over a range extending from the lowest temperature up to the melting-point. As a matter of fact, three such series of observations were made on different days, and showed no systematic disagreement among themselves.

The mercury used in this work was distilled three times in a slow current of air of about 30 mm. pressure in the manner described by Hulett *. This method of purification is stated by him to be very effective as regards the removal of both base and noble metals. We took a heating curve of our purified mercury, allowing the cooled solid to heat up slowly in a Dewar flask, and recorded its temperature as a function of time. The curve so obtained showed a very sharp and quite horizontal arrest at the melting-point, followed by a sharp break when melting was complete. Hence we consider that a satisfactory purity was attained. The platinum thermometer was calibrated at the steam-point, the ice-point, the melting-point of mercury, and the boiling-point of liquid oxygen, and the resistance formula of Van Dusen † was employed.

Calculation of the Expansion Coefficient.

The method of calculating the results was as follows:— The volume of the dilatometer bulb at room temperature was found by weighing it full of liquid mercury, and the volume at lower temperatures was calculated, using the coefficient of expansion of pyrex which is known over the range from $-170°$ to $+30°$ C. from the work of Buffington and Latimer ‡. The volume per cm. length of the capillary stem was found by similar methods, and proved to be uniform over its working length. The volume of solid mercury actually in the bulb during a determination of expansion coefficient was deduced from a knowledge of of its mass, and the fact that, under zero external pressure, 1 c.c. of mercury at 0° C. (whose mass is 13·596 grams) becomes 0·99298 c.c. at $-38·8°$ C., and changes its volume by 0·03447 c.c. on freezing §. This leads to a value of 14·182 for the density of the solid at its melting-point. Knowing the volume of the solid at its melting-point, a very rough value of the expansion coefficient was all that was necessary to deduce its volume at the temperature of experiment with sufficient accuracy for our purpose.

* Phys. Rev. xxxiii. p. 307 (1911).
† Am. Chem. Soc. Journ. xlvii. p. 326 (1925).
‡ Am. Chem. Soc. Journ. xlviii. p. 2305 (1926).
§ Bridgman, Am. Acad. Sci. Proc. xlvii. p. 343 (1911).

Knowing the volume of the solid mercury and the volume of the dilatometer bulb, the volume of alcohol in the "dead space" was obtained by subtraction.

In reducing the data of a typical determination we plotted the height of the meniscus as read by the cathetometer and the resistance of the platinum thermometer both as functions of time on a single piece of large graph paper, drew a smooth curve through the experimental points, and read off from the curves the corresponding heights and resistances at two definite times. Hence we obtained the increase in volume of alcohol in the capillary corresponding to a known increase of temperature of the dilatometer. It was necessary to apply three corrections to this increase of volume of alcohol before the increase in volume of mercury could be deduced:

(1) Allowance had to be made for the increase of volume of the alcohol in the bulb, due to its own expansion. For this purpose we used the results of Seitz and Lechner as quoted in Landolt-Börnstein's Tables.

(2) The thermal expansion of the pyrex bulb had to be taken into consideration. This correction, which was quite small, was made using the data of Buffington and Latimer *.

(3) The rise in the height of the alcohol meniscus was increased owing to the fact that alcohol which was originally in the dilatometer was in effect transferred from there to the free air, and its temperature thereby increased. Correction for this effect was made by multiplying the observed increase in height by the ratio of the densities at air temperatures and at the temperature of the dilatometer bulb respectively.

Correction (1) was the most considerable in magnitude, since the expansion coefficient of ethyl alcohol is about six times that of solid mercury. As it was important to be sure that our ethyl alcohol had the same expansion coefficient as that observed by Seitz and Lechner, we made a separate determination of this quantity at a mean temperature of $-41°$ C., and obtained agreement within 2 per cent. The most conclusive evidence on this point, however, is the fact that we made three sets of determinations of the expansion of solid mercury with different volumes of alcohol-filled "dead space," the contribution of the alcohol to the total observed expansion ranging from 50 to 20 per cent. There was, however, no systematic difference between the values

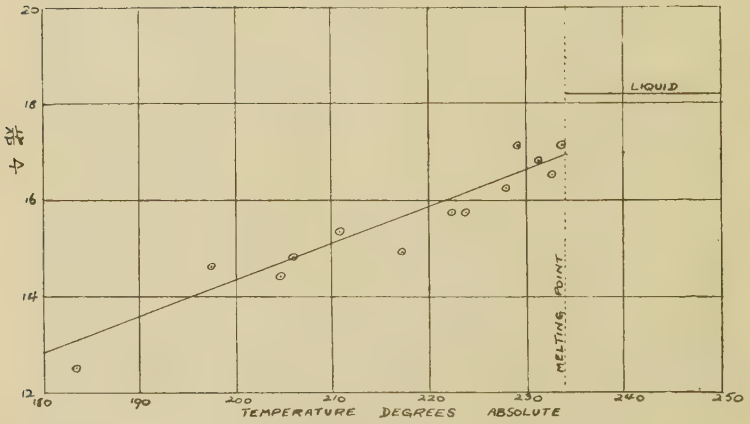
* *Loc. cit.*

for the expansion of mercury deduced from the three sets of experiments.

Table I.

Absolute Temperature.	$\frac{1}{V}\frac{dV}{dT}\times 10^5$.
183·3	12·5
197·3	14·6
204·5	14·4
205·6	14·8
210·6	15·3
217·1	14·9
222·4	15·7
223·7	15·7
227·9	16·2
229·0	17·1
231·1	16·8
232·6	16·5
233·7	17·1
234·3	Melting-point.

Fig. 2.



The values of the cubical expansion coefficient as experimentally determined are given (multiplied by 10^5) in Table I. and plotted in fig. 2. The variation of expansion coefficient with temperature over the range covered by our experiments has been represented by a straight line, as we feel that

our data are not sufficiently extensive to justify drawing it otherwise. It will be noticed that the greatest deviation of an individual point from the mean curve is about 4 per cent., and we estimate that the mean curve is certainly within 3 per cent. of the true values.

As a general check on the accuracy of the work the agreement of our value for the expansion coefficient of ethyl alcohol with that of Seitz and Lechner may be cited. Further, we made a rough determination of the expansion of liquid mercury just above the melting-point by the same method as that used for the solid, and obtained a value for $\frac{1}{V}\frac{dV}{dT}$ which agreed within 4 per cent. with the value $18{\cdot}2\times10^{-5}$ calculated from Bridgman's data * for liquid mercury under zero external pressure.

The Atomic Heat of Mercury.

In fig. 3 the values of C_p, the atomic heat at constant pressure (as determined by C. & S.), have been plotted as a function of absolute temperature. In order to obtain the atomic heat at constant volume we have used the well-known thermodynamic relation

$$C_p - C_v = \frac{\alpha^2 VT}{\kappa},$$

in which α is the coefficient of cubical expansion, V the atomic volume, T the absolute temperature, and κ the compressibility. The values of α have been obtained from fig. 2, while V for the solid just below its melting-point is $14{\cdot}14\left(i.e., \frac{200{\cdot}6}{14{\cdot}182}\right)$.

In a plate in the paper already quoted † Bridgman gives the initial slope of the isothermal for solid mercury at the melting-temperature, but says that it has been obtained by an approximate computation and not by direct experiment. This leads to a value of $3{\cdot}38\times10^{-6}$ cm.^{2}/kgm. for κ, a value which is unlikely to be in error by more than 5 per cent. at the outside, because Bridgman says elsewhere in the paper ‡ that the compressibility of the solid at the freezing-point is less than that of the liquid, the difference being in the neighbourhood of 10 per cent., and the compressibility of the liquid was directly determined with great accuracy.

* *Loc. cit.* p. 432.
† *Loc. cit.* opposite p. 438.
‡ *Loc. cit.* p. 423.

The variation of κ with temperature is not known for the solid, but it is in general small. In the case of cadmium *, for instance, there is an increase of 3 per cent. over the temperature range 30° to 75° C. We have therefore taken $\frac{V}{\kappa}$ to be constant, a procedure which will not introduce large error, especially as V itself naturally increases slightly with temperature. In any case the value we have taken will be correct at the melting-point. The calculated values of

Table II.

Absolute Temperature.	$C_p - C_v$.
190	0·342
200	0·402
210	0·468
220	0·542
230	0·621
234	0·655

Table III.

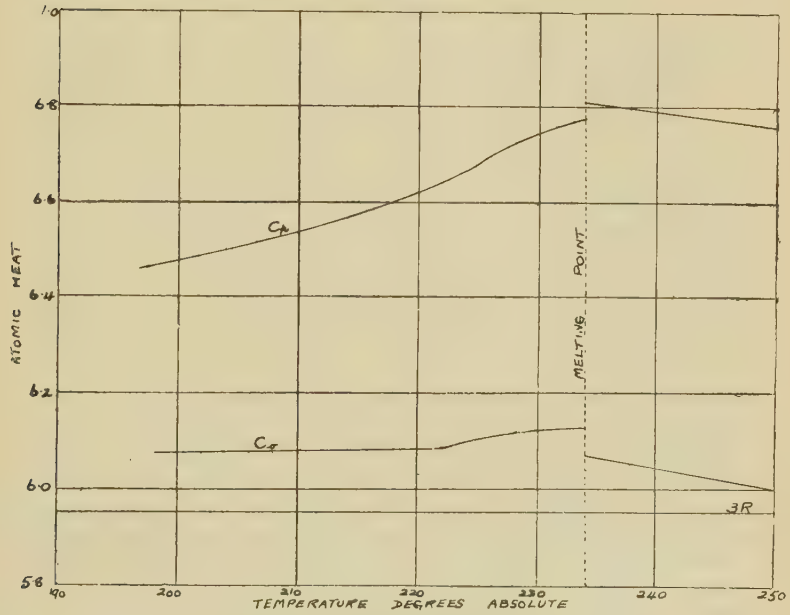
Absolute Temperature.	C_v.
200	6·08
205	6·08
210	6·08
215	6·08
220	6·09
225	6·10
230	6·13
234	6·13

$C_p - C_v$ in calories per gram molecule are given in Table II., and the resulting values of C_v are given in Table III. and plotted in fig. 3. The values of C_v for the liquid, computed in a former paper †, have also been plotted. One sees that from 200° A. to 220° A. C_v remains practically constant, but that the curve rises rather suddenly at slightly above 220° A. and subsequently becomes horizontal at the melting-point at a value of 6·13.

* Bridgman, Am. Acad. Sci. Proc. lviii. p. 215 (1923).
† C. & S. p. 258.

Before drawing any conclusions it is necessary to discuss the accuracy of the data. The percentage accuracy of C_v depends on the precision with which C_p has been determined and on the accuracy of the $C_p - C$ correction. Now C_p is certainly accurate to within 1 per cent. *. With regard to $C_p - C_v$, the only factors likely to be in error are α and κ. We have already decided that α is correct to 3 per cent. and κ to 5 per cent. Hence the maximum possible error in

Fig. 3.



$C^p - C_v$ would be about 11 per cent., producing an error of 1 per cent. in C_v at the melting-point.

Assuming, then, that all possible sources of error chance to add, C_v would still be correct within 2 per cent. Actually, however, C_v exceeds 3R by 3 per cent. at the melting-point, and the effect therefore seems to be too large to be accounted for by experimental error. The theoretical significance of the excess of C_v above 3R near the melting-point has already been discussed in a former paper †, and

* C. & S. p. 256.
† C. & S. p. 261.

it has been suggested that it is due in part at least to anharmonic atomic vibrations.

Further investigations on other elements are in progress.

In conclusion, it is a pleasure to express our thanks to Prof. H. Stansfield for his kind interest in the work.

Feb. 28th, 1931.

XLVI. *On the Turbulent and Stream-line Damping of a Pendulum in Viscous Media.* *By* G. W. Brindley, *M.Sc.*, *Assistant Lecturer in Physics at the University of Leeds* *.

1. *Introduction.*

THE theory of the motion of a pendulum consisting of a sphere suspended by an infinitely fine wire in a viscous liquid has been given by Stokes † and by Kirchhoff ‡, the main assumption involved in the theory being that the motion shall be so slow that turbulence will not arise, and that the damping of the motion shall be due entirely to the viscosity of the medium, and therefore proportional to the first power of the velocity. Hoare § appears to have been the first to draw attention to the fact that at ordinary amplitudes, of the order of 1 cm. for pendulums several hundred centimetres long, Stokes's theory is not in accordance with observation, for, whereas the theory requires the logarithmic decrement of the motion to be constant, in practice the decrement is found to vary, becoming smaller as the amplitude decreases. This problem has been examined experimentally by the writer and Emmerson‖ recently, and it has been found that, provided the amplitudes are sufficiently small, of the order of 1 mm., the log-decrement is constant, a result which is qualitatively in agreement with Stokes's theory. The motion is then so slow that, following Prandtl, it may aptly be described as "creeping" motion. A further assumption involved in the theory is that the suspension contributes inappreciably to the damping. In practice this is not the case, because, if a pendulum is swung with one, two . . . . dummy suspension wires mounted parallel to and

* Communicated by Prof. R. Whiddington, D.Sc., F.R.S.

† G. G. Stokes, 'Mathemathical and Physical Papers,' iii. p. 34.

‡ G Kirchhoff, 'Mechanik,' ch. xxvi.

§ F. E. Hoare, Phil. Mag. viii. p. 899 (1929); ix. p. 502 (1930).

‖ G. W. Brindley and T. Emmerson, Phil. Mag. xi. p. 633 (1931).

fixed rigidly to the real suspension wire, as described by the writer and Emmerson (*loc. cit.*), the log-decrement increases linearly with the number of wires. In this way an estimate based on purely experimental data was made for the damping due to the suspension wire, and hence a correction was applied to the damping of the pendulum to obtain the true damping for the sphere. The coefficient of viscosity of the medium, water, was calculated from this result, and the value obtained agreed with the standard value to within 1 per cent.

Two definite conclusions can be drawn from these results. Firstly, Stokes's theory of the motion of a pendulum is quantitatively true at amplitudes which are sufficiently small, generally of the order of 1 mm. Secondly, the damping due to the suspension wire, however fine this may be, is appeciable in all practical cases, and may be estimated in two ways ; experiments may be made with one, two, and three suspension wires in turn, as described previously, or the results of the previous experiments may be accepted and the theoretical damping given by Stokes's theory for the sphere alone be subtracted from the experimental damping for the sphere and wire together. The latter method will be used in the present paper.

The previous paper by the writer and Emmerson was devoted mainly to examining under what conditions Stokes's theory is valid. There are still a number of questions to which no satisfactory answers appear to have been given. The main outstanding question is why, at amplitudes larger than a few millimetres, does Stokes's law break down? Is the discrepancy between theory and experiment due to some complication arising from the wire disturbing the free flow of liquid round the oscillating sphere, or is it due to the resistance to the motion of the sphere depending on some power of the velocity other than the first? In what follows, these and related questions will be considered from the experimental standpoint, and an explanation will be suggested which appears to account for the observed facts.

2. *An Outline of the Theory of Stream-line Damping for Creeping Motion.*

The equation of motion of a pendulum consisting of a sphere of mass M and radius r oscillating in a medium of density ρ and viscosity η is given by Stokes as

$$(\mathrm{M}+k\mathrm{M}')\frac{d^2\alpha}{dt^2}+\frac{9\pi}{2\mathrm{T}}k'\mathrm{M}'\frac{d\alpha}{dt}+(\mathrm{M}-\mathrm{M}')\frac{g}{l}\alpha=0. \quad (1)$$

In this equation

$$k = \left(\frac{1}{2} + \frac{9}{4\beta r}\right),$$

$$k' = \left(\frac{1}{\beta r} + \frac{1}{\beta^2 r^2}\right),$$

$$\beta = \sqrt{\frac{\pi\rho}{\eta T}};$$

also α = amplitude of the sphere at time t,
T = periodic time in the medium,
M′ = mass of the medium displaced by the sphere,
l = length of the pendulum.

Equation (1) represents a damped oscillation, and if the logarithmic decrement λ is defined as the logarithmic ratio of successive amplitudes on opposite sides of the zero, and therefore corresponding to a time interval of $\frac{1}{2}$T, then

$$\lambda = \frac{9\pi k' M'}{8(M + kM')}. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Now, in connexion with results which are given later, it is of interest to consider how the amplitudes will decay for a number of pendulums having the same period T, oscillating in the same medium, but having different sized spheres of the same density. Since for these pendulums r is the only variable, and since for creeping motion the resistance is proportional to the velocity, which is proportional to the amplitude α, we can write for the decay of amplitude with time,

$$\frac{d\alpha}{dt} = -\text{const.}\, f(r) \,.\, \alpha. \quad . \quad . \quad . \quad (3)$$

The solution of this equation is

$$\alpha = c_0 e^{-\text{const.}\, f(r)\,.\,t}; \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

but, since the log-decrement is λ, we have also

$$\alpha = \alpha_0 e^{-\lambda \cdot \frac{2 \cdot t}{T}}. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Hence, from (4) and (5),

$$\text{const.}\, f(r) \equiv \frac{2}{T}\lambda,$$

and since T is being kept constant,

$$f(r) = \text{const.}\, \lambda. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The form of $f(r)$ can be obtained from (2) by substituting for k and k', and then, following Hoare, assuming $\left(\frac{1}{\beta^2 r^2}\right)$ is negligible compared with $\left(\frac{1}{\beta r}\right)$ and 2λ negligible compared with π, both of which are justified for the conditions of the experiment, we obtain

$$\eta = \frac{16r^2}{81\pi}\left[2\left(\frac{M}{M'}\right)+1\right]^2\left(\frac{\lambda^2}{T}\right). \quad . \quad . \quad . \quad (7)$$

If σ is the density of the spheres, then $\frac{M}{M'} = \frac{\sigma}{\rho}$, which is constant. Hence, from (7),

$$\lambda = \text{const.}\left(\frac{1}{r}\right). \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Combining (6) and (8),

$$f(r) = \text{const.}\left(\frac{1}{r}\right).$$

Hence the law of decay of amplitude for a set of pendulums, such as we are considering, which differ only as regards the sizes of the spheres, is the following, within the limits for which equation (7) is valid :

$$\frac{d\alpha}{dt} = -\text{const.}\left(\frac{\alpha}{r}\right). \quad . \quad . \quad . \quad . \quad . \quad (9)$$

3. *Comparison with Experiment.*

From (9)

$$-r\left(\frac{d \cdot \log \alpha}{dt}\right) = \text{const.} \quad . \quad . \quad . \quad . \quad (9a)$$

i. e., $r\lambda = \text{const.}$

This is completely verified in practice ; the results given in Table I. are taken from the paper by Brindley and Emmerson (*loc. cit.*) :—

TABLE I.

Diameter of sphere.	λ.	$r.\lambda$.
6·35 cm.	0·0187	$0·059_5$
7·62 „	0·0152	0·058
14·61 „	$0·0078_7$	$0·057_5$

4. *Damping for Turbulent Motion.*

The general nature of turbulent damping can be considered as follows *:—Whenever there is transference of momentum in a fluid from faster to slower moving layers, stresses are set up. In cases of laminar flow, as in the slow flow of a liquid through a tube, momentum is transferred by molecular collisions, and the viscous forces which arise are explained by the kinetic theory in terms of the mean free path of the molecules. In turbulent flow transference of momentum occurs between masses of liquid, that is to say, between large groups of molecules rather than between individual molecules. The main characteristics of turbulent flow are, firstly, that pressure differences are not proportional to the first power of the velocity, but increase more quickly; secondly, the flow is not stationary, since the pressure and the velocity do not remain constant at a particular point, but oscillate about a mean value; thirdly, if the velocity at any point be resolved into two components u and v, and if the mean value $\bar{u}$ is either small or not very variable from layer to layer of the liquid, and if $\bar{v}=0$, then the average stress at the point considered is of the form

$$\tau=\rho\,\overline{uv}.$$

From this it is inferred that, when turbulence occurs, the stresses which arise are proportional to the square of the velocity, and, therefore, when a body moves through a liquid producing turbulence, the resistance to motion should be proportional to the square of its velocity. Allen † has carried out experiments on the resistance experienced by spheres moving under gravity with their terminal velocities in various liquids for values of Reynolds's number between 0·1 and 4.10^3, and for the larger values of Reynolds's number the v^2-law was verified.

For a pendulum, Reynolds's number for the maximum velocity, when the amplitude is α and the period T, is given by

$$\mathrm{R}=\frac{\rho r}{\eta}\,.\,v_{\max.}\qquad\text{and}\qquad v_{\max.}=\frac{2\pi}{\mathrm{T}}\,\alpha,$$

whence

$$\mathrm{R}=\frac{\rho r}{\eta}\,.\,\frac{2\pi}{\mathrm{T}}\,.\,\alpha.$$

* *Cf.* L. Hopf, "Zähe Flüssigkeiten," *Handbuch der Physik*, vii. p. 125 (1927); also L. Prandtl, 'The Physics of Solids and Fluids,' ch. vi. p. 279 (1930).

† H. S. Allen, Phil. Mag. (5), l. p. 323 (1900).

For a sphere of radius 2·54 cm. oscillating in water with a period of 2·56 seconds and with an amplitude of 1 cm., R = 528. Hence, for oscillations between 1 cm. and 5 cm., R varies between $0{\cdot}5 \times 10^3$ and $2{\cdot}5 \times 10^3$. For this range of values of Reynolds's number it would be expected that the v^2 law of resistance would be true.

The rate of decay of amplitude of a pendulum will be proportional to the resistance experienced by the sphere, and will depend also on the size and the inertia of the sphere. Since v is proportional to α, and since for a set of spheres of the same density both the size and the inertia depend on r, we may write

$$\frac{d\alpha}{dt} = -\text{const.} f(r)\alpha^2, \quad . \quad . \quad . \quad . \quad (10)$$

whence

$$\frac{d \,.\, \log \alpha}{dt} = -\text{const.} f(r) \,.\, \alpha. \quad . \quad . \quad . \quad . \quad (10\,a)$$

We may compare this with the expression $(9\,a)$ for stream-line damping,

$$\frac{d \,.\, \log \alpha}{dt} = -\text{const.} \left(\frac{1}{r}\right).$$

These equations enable us to distinguish easily between stream-line and turbulent damping experimentally. If we plot $\log \alpha$ against n, the number of swings, then we should obtain a straight line for stream-line damping and a curve for turbulent damping. Also, if we plot $\frac{d \log \alpha}{dn}$ against α, a straight line parallel to the α-axis should be obtained for stream-line damping and also a straight line for turbulent damping with a gradient $-\text{const.} f(r)$ if equation $(10\,a)$ is correct. Further, by studying the gradients for different values of r, it should be possible to determine the form of $f(r)$. It is of importance to observe that if $\left(\frac{d\alpha}{dt}\right)$ in equation (10) depends on any other power of α than the second, $\left(\frac{d \log \alpha}{dt}\right)$ will not vary linearly with α.

5. *Experimental Details.*

In order to measure the amplitudes with sufficient accuracy, the following methods have been used. For the largest amplitudes between 10 cm. and 1 cm. a metre scale

was placed behind the wire of the pendulum and the amplitudes were recorded directly. To increase the accuracy it was found necessary to repeat a series of readings about six times under identical conditions. As steel spheres were used throughout, a magnetic device was employed for starting the oscillations, and in this way any required number of readings could be obtained under absolutely identical conditions. For smaller amplitudes, between 3 cm. and 0·3 cm., a telescope with an eyepiece scale was used, while for the smallest amplitudes, between 0·2 cm. and 0·02 cm., a microscope with an eyepiece scale was used. The precautions essential for the measurement of very small amplitudes have been described previously.

6. *Results.*

The results obtained indicate that the damping of the oscillations can be regarded as occurring in several stages. For the first two or three oscillations, when the amplitude is of the order of 10 cm., the damping is very large indeed, and obviously arises from several causes. Apart from the turbulent damping due to the passage of the sphere through the medium (usually water), surface-ripples were formed by the wire moving through the surface, and, moreover, for these oscillations, the sides of the tank employed certainly restricted the free flow of the water, as was shown by very simple tests.

After the first few oscillations the results indicate that there is a period when the motion is turbulent and when the damping due to the formation of surface-ripples and to the finite size of the medium is negligible. For a range of, roughly, twenty oscillations, equations (10) and (10 a) represent correctly the nature of the damping.

There is then a short transition stage, when neither equation (9 a) nor equation (10 a) holds, which is then followed by a final stage for which as many as 50 oscillations have been measured, for which the damping is truly stream-line, and for which equation (9 a) holds good. The intermediate transition stage between stream-line and turbulent damping has also been observed by Allen (*loc. cit.*). For a pendulum, where the velocity is periodic, a sharp break between turbulent and stream-line flow would not be expected.

The results obtained can be given most concisely in graphical form. In fig. 1 a typical set of results is given for a steel sphere of diameter 2 in. oscillating in water with

a period of 2·56 seconds. Values of $\log_{10}\alpha$ are plotted against n, the number of oscillations measured on one side only of the zero. Since all the experimental points lie either exactly on the curves drawn or so near that the difference is too small to be shown in the figure, it was considered unnecessary to show the actual experimental points. The data given in the figure cover a very wide range of amplitudes from 10 cm. to 0·04 cm. To enable the actual amplitudes to be visualized more easily, a scale of values of α is given parallel to the $\log_{10}\alpha$ values.

In the upper part of fig. 1 the portion of the curve marked "*a*" was obtained by measuring the amplitudes directly with a metre scale; the readings for the part marked "*b*" were obtained with a telescope; while for the very small amplitudes given in the lower part of the figure, marked "*c*," the readings were obtained entirely with a microscope. The lower curve corresponds to stream-line damping for which Stokes's theory holds, and the results given below indicate that the upper curve depends on turbulent damping. The broken line in the upper part of the figure is drawn parallel to the line "*c*"; it enables one to see rather more easily how the turbulent damping departs from the stream-line damping.

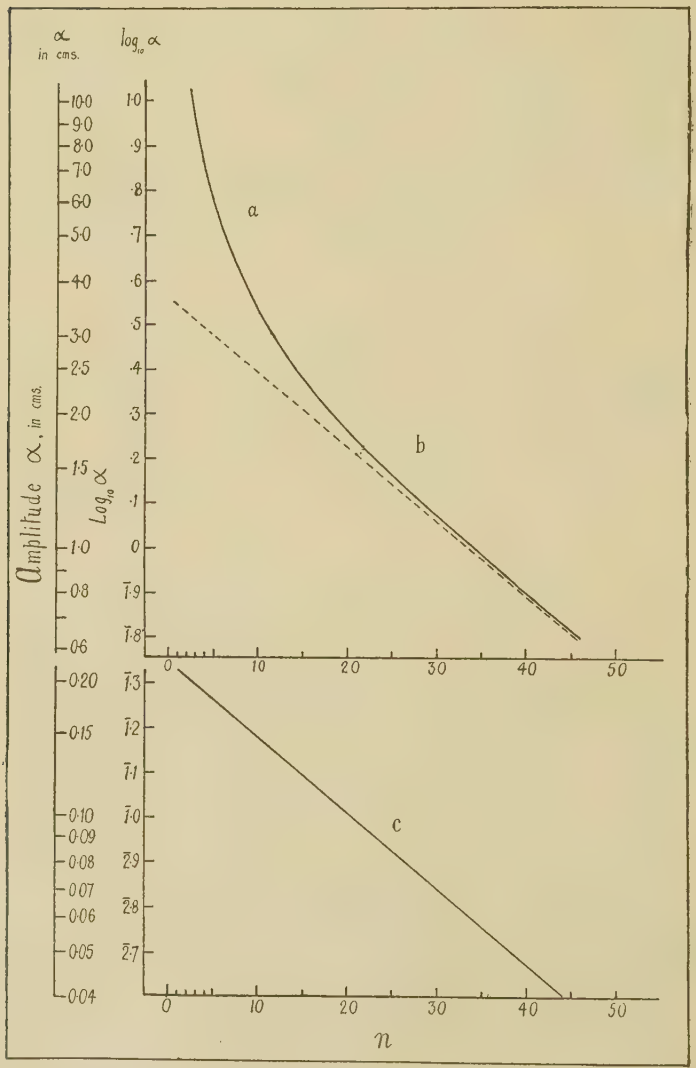
7. *A Consideration of the Experimental Results in Detail and the Form of the Function $f(r)$ in Equation* (10).

Results have been obtained with three spheres, all of them being of polished steel of the same density, with diameters 2 in., $2\frac{1}{2}$ in., and 3 in. In all three cases the pendulums had the same period in water, 2·56–2·58 seconds, so that time-intervals can be measured in terms of n, the number of complete oscillations, more conveniently than in terms of t, and we can substitute $\frac{d}{dn}$ for $\frac{d}{dt}$. In order to obtain equal periods it was only necessary to keep the distance from the point of suspension to the centre of the spheres constant, since the effect of the change of damping for different spheres on the period is negligible.

Curves similar to those given in fig. 1 were obtained for each of the three pendulums. Values were then obtained graphically for $\frac{d\log_{10}\alpha}{dn}$ for the complete range of values of α which were measured. A typical set of results is shown in fig. 2 for the 2 in. sphere.

In order to obtain $\frac{d \log_{10} \alpha}{dn}$ sufficiently accurately it was

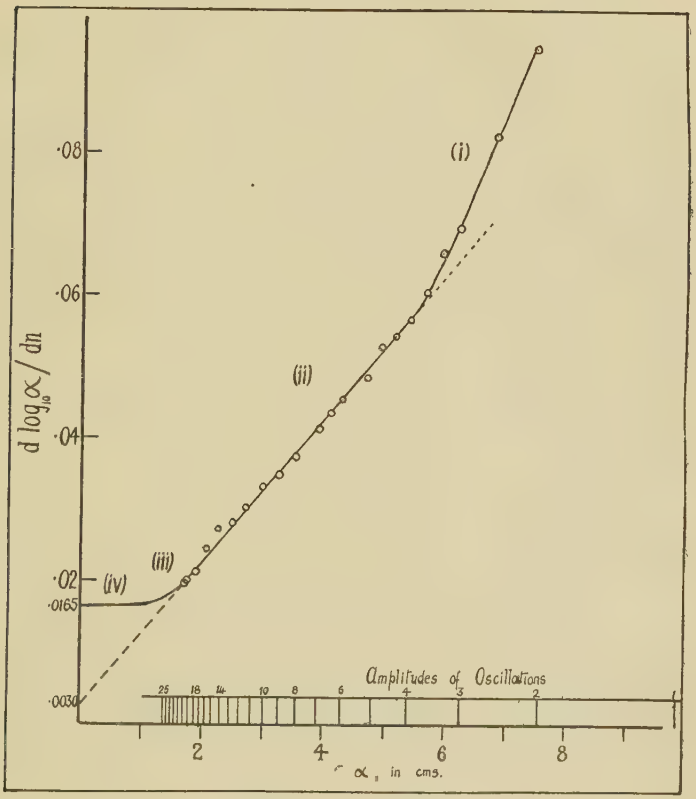
Fig. 1.



found essential to draw the $\log_{10} \alpha$, n curves on a very large scale, and considerable care was necessary in the drawing of the tangents. In fig. 2 the calculated points are shown, so

that it will be seen what degree of accuracy is possible in constructing the $\frac{d \log_{10} \alpha}{dn}$, α curve. The amplitudes of the larger oscillations are also indicated in the figure.

Fig. 2.



In discussing the results it is convenient to divide the curve in fig. 2 into four parts. The first part of the curve depends on the first three oscillations, for which the damping is very large, being due to turbulence, the formation of surface-ripples, the restricted movement of the water by the sides of the tank, and possibly other causes as well. The second part of the curve, which corresponds to about twenty oscillations, agrees with equation (10 a). The damping of these oscillations is due to the turbulence produced by the

sphere, and the gradient of this part of the curve depends on $f(r)$ in equation (10). The third part is the transition stage, and the fourth part, for which about fifty oscillations have been measured, depends on stream-line damping.

Now equation (10 *a*) would lead us to expect that $\frac{d \log \alpha}{dn}$ would tend to zero as $\alpha \to 0$. This was found to be *approximately* true for all three pendulums. In fig. 2 $\frac{d \log \alpha}{dn}$ for the second part of the curve is extrapolated to smaller amplitudes, and it is seen that the broken line passes *almost* through the origin. The explanation of this must be that, apart from the turbulent damping of the sphere in the region marked (ii), there is also some constant damping, which probably arises from the suspension wire.

It seems very probable, therefore, that the damping due to the suspension wire, which presumably is stream-line damping, since Reynolds's number for the wire is so much smaller than for the sphere, can be obtained by observations in the turbulent region. By comparing the damping for the wire obtained in this way with the damping obtained by the methods described in the first section of this paper, it should be possible to get a good check of the correctness of equations (10) and (10 *a*).

The following results have been obtained :—

For the pendulum with a 2 in. sphere, from the conditions of the experiment we have

$$\eta = 0{\cdot}0115, \qquad \rho = 1{\cdot}0, \qquad T = 2{\cdot}56 \text{ sec.},$$
$$r = 2{\cdot}54 \text{ cm.}, \quad M = 535 \text{ gr.}, \quad M' = 66 \text{ gr.}$$

Substituting these values in equation (2),

$$\lambda = 0{\cdot}0161 ;$$

then, from equation (5),

$$\frac{d \log_{10} \alpha}{dn} = 0{\cdot}0140.$$

Experimentally, at very small amplitudes, the following results were obtained :—

$$\left.\begin{aligned} \frac{d \log_{10} \alpha}{dn} &= 0{\cdot}0164 \\ &\quad 0{\cdot}0163 \\ &\quad 0{\cdot}0166 \\ &\quad 0{\cdot}0167 \end{aligned}\right\} \text{ mean value} = 0{\cdot}0165.$$

Hence the stream-line damping for the sphere alone ..... $= \underline{0{\cdot}0140}$

The stream-line damping for sphere and wire ..... $= \underline{0{\cdot}0165}$

Then stream-line damping for the wire alone..... $= \underline{0{\cdot}0025}$

Now, by extrapolating from the *turbulent* region in fig. 2, we find at $\alpha = 0$,

$$\frac{d \log_{10} \alpha}{dn} = \underline{0{\cdot}0030.}$$

As the probable error in the experimental measurements is of the order of 1 per cent., the agreement between these two estimates for the damping due to the wire is very close indeed. Results equally good have also been obtained for the $2\frac{1}{2}$ in. and 3 in. spheres.

TABLE II.

Sphere.	r cm.	r^2.	$\frac{d}{d\alpha}\left(\frac{d \log_{10} \alpha}{dn}\right)$.	$r^2 \cdot \frac{d}{d\alpha}\left(\frac{d \log_{10} \alpha}{dn}\right)$.
2 in.	2·54	6·45	0·0140	0·090
$2\frac{1}{2}$ in.	3·17	10·05	$0{\cdot}0086_6$	0·087
3 in.	3·81	14·52	$0{\cdot}0062_9$	0·091

The close agreement between the results obtained for the wire when the pendulum is being damped by turbulence and when the damping is stream-line points to equation (10) being of the right general form.

It is of interest next to compare the turbulent damping of the three pendulums and so to determine the form of $f(r)$ in equation (10). We have

$$\frac{d \log_{10} \alpha}{dn} = -\text{const.} f(r) \cdot \alpha.$$

Then

$$\frac{d}{d\alpha}\left(\frac{d \cdot \log_{10} \alpha}{dn}\right) = -\text{const.} f(r).$$

The experimental results are in keeping with the relation

$$r^2 \cdot \frac{d}{d\alpha}\left(\frac{d \log_{10} \alpha}{dn}\right) = -\text{const.} \quad . \quad . \quad . \quad (11)$$

The results given in Table II. show that within the limits

of experimental error equation (11) represents the observed facts. Over the range of values of r which has been used

$$f(r) = \frac{1}{r^2}.$$

Hence, from equation (10), the law for the decay of amplitude of a pendulum when turbulence occurs is of the form

$$\frac{d\alpha}{dt} = -\text{const.}\left(\frac{\alpha}{r}\right)^2;$$

for stream-line damping the law of decay is

$$\frac{d\alpha}{dt} = -\text{const.}\left(\frac{\alpha}{r}\right).$$

To both these expressions for $\frac{d\alpha}{dt}$ a constant must be added for the damping due to the suspension wire.

Finally, I would like to thank Prof. Whiddington for his interest in the work.

8. *Summary.*

The conditions under which Stokes's theory of the motion of a pendulum is correct are discussed. Experimental results show that the damping due to the suspension wire is important, and methods of obtaining it are briefly considered. At amplitudes larger than a few millimetres for pendulums several hundred centimetres long, Stokes's law is no longer true, since the damping ceases to be due to stream-line motion of the liquid. The nature of turbulent damping is considered, and it is shown that at larger amplitudes the resistance to motion depends on a v^2-law. Experimental results are given for a number of pendulums having the same period but with different spheres, all of the same density. For a set of pendulums of this kind the law for the decay of amplitude at small amplitudes, where stream-line damping occurs is

$$-\frac{d\alpha}{dt} = \text{const.}\left(\frac{\alpha}{r}\right),$$

and at large amplitudes, where turbulent damping occurs, is

$$-\frac{d\alpha}{dt} = \text{const.}\left(\frac{\alpha^2}{r^2}\right).$$

For the range of conditions investigated it is shown that both these laws are obeyed to within a few per cent.

The Physics Department,
University of Leeds,
March 1931.

XLVII. *Frictional Electric Charges upon the Surfaces of Single Metal Crystals.* *By* P. A. Mainstone, *M.Sc., Lecturer in Physics, University College of North Wales* *.

IN a previous paper † the author described some measurements of the frictional charges produced by very light rubbing upon the surfaces of metals under varying gas pressure. A characteristic variation of the charge with gas pressure was observed, and it was concluded that only at the lowest obtainable pressure was the charge characteristic of the rubbing surfaces.

The present paper describes measurements of this type made with single crystals of aluminium and copper. The friction chamber was as described in the previous paper, and all the measurements were made at the lowest pressure obtainable by the use of charcoal and liquid air. Mercury vapour was excluded from the apparatus, the pressure being tested by a Pirani gauge.

The aluminium crystal, in the form of a test-piece 19 mm. in diameter, was kindly supplied by Prof. E. A. Owen. For the copper crystal, in the form of a rod $6\frac{1}{2}$ mm. in diameter, the author is indebted to Prof. Sir Harold Carpenter. In each case a thin normal section was cut, and the positions of the crystalline axes determined from a Laue diagram. No difficulty was experienced in the case of aluminium, but in the case of copper several sections had to be cut before a successful photograph was obtained.

For each crystal, surfaces were cut as nearly as possible along the (100), (110), and (111) planes respectively. The crystal was fixed in a suitable holder, and by means of two angular settings, corresponding to rotations about horizontal and vertical axes respectively, the required plane could be brought into a vertical position, the crystal then being cut by means of a small and thin circular saw. In the case of the aluminium crystal it was possible to cut a specimen which could be turned down to a cylinder about 7 mm. in thickness and 17 mm. in diameter. By solution in hot caustic soda these dimensions were then reduced to a thickness of about 5 mm. and a diameter of 15 mm. By this means it was hoped to reduce as far as possible the surface deformations caused by the cutting-tools. A similar procedure was adopted with the copper crystal,

* Communicated by Prof. E. A. Owen, M.A., D.Sc.

† Phil. Mag. (7) viii. pp. 733–749.

but in this case the surface was approximately rectangular, and of dimensions about 15 mm. by 5 mm. A surface layer was removed by solution in nitric acid, although the reduction in thickness was not so great as in the case of aluminium.

Each aluminium specimen in turn was fixed as accurately as possible in the same position on the insulating base, the two auxiliary metal surfaces being formed of ordinary polycrystalline aluminium. The rubber was the original glass disk attached to a small ebonite block, the total mass being only 1·5 gram. The procedure adopted was as follows:— The three co-planar surfaces were rubbed down to the

Table I.—Aluminium.

Capacity of System, 350 cm.

	Potential in volts generated per single rub.							
	Surface polished.				Surface progressively etched.			
	1.	2.	3.	4.	1.	2.	3.	4.
Polycryst.	23	17·5	27	20	21	23	13	27
(100)	22	29	15	17	17	31	22·5	27
(110)	22	19	28	16	23	25	16	26
(111)	20	21·5	33	19	22	20	37	36

No. 000 emery stage, the specimen proper then being removed, polished, and replaced. At the low pressure the charge per rub increased to approximately a steady value only after several hundred rubs. Generally about 500 rubs were made, and a similar number after an interval of two or three hours. In general the charge per rub had definitely reached a steady value at or before this stage. This set of readings was repeated two or three times, the specimen being lightly etched with caustic soda and repolished before each repetition. Further readings were obtained with the surface progressively etched without any subsequent polishing.

The results for the three surfaces of the single crystal of aluminium, together with similar results for a polycrystalline surface, are shown in Table I. The charge on the metal was in all cases negative.

A given set of readings is seen to be fairly consistent on repetition, although occasionally an abnormal set was obtained. It is clear that, except in the case of the (111) face, no definite variation in the charge can be observed. Fifth and sixth progressive etchings were given in this case only, and the potential appeared to remain steady at 36 volts. If each surface were truly plane, it might be expected that the charge, for the etched surface at least, would depend upon the number of surface atoms in a given area. This number is greatest for the (111) and least for the (110) face. The result for the etched (111) face could be explained on this view, but it can hardly be claimed from

TABLE II.—Copper.

Capacity of System, 1500 cm.

	Potential in volts generated per single rub.						
	Surface polished.				Surface progressively etched.		
	1.	2.	3.	4.	1.	2.	3.
Polycryst.	3	3	6·5	6	2·5	2	—
(100)	2	5	5	4·5	1·25	2·5	1·5
(110)	5·5	3·5	8	8	2·5	0·75	0·75
(111)	3	2·5	1·75	2·25	1	2·25	1

this isolated case that any definite variations in the frictional charges upon the different surfaces have been established.

The accuracy with which each surface was cut was subsequently tested by means of the ionization spectrometer. Each specimen was mounted in two positions in turn such that the direction of rubbing lay horizontally and vertically respectively. Each gave the expected reflexion, and with one exception the error in cutting was not more than about 1°. In the case of the (111) face an error of 4° was found in a direction perpendicular to that of rubbing.

The results for copper, obtained by a similar procedure, are given in Table II.

Each specimen was fixed so that rubbing took place along its greater dimension. The effect of etching with nitric acid

was, in most cases, very marked, the charge diminishing rapidly on progressively etching. No increase in charge on the etched (111) face was observed in this case, the greatest charge appearing on the polished (110) face. The separate faces were tested on the ionization spectrometer as before, and although the accuracy of cutting was not quite so great as in the case of aluminium, the average error was not more than about 2°.

The experiments cannot be said to have shown any marked differences between the tribo-electric effects upon the various faces of a single metal crystal, or between polycrystalline and single crystal surfaces. The difference between etched and polished surfaces was pronounced in the case of copper, but not in the case of aluminium. The etched copper surface may possibly offer fewer points of contact with the rubber than does the polished surface. The failure to differentiate between the various surfaces is almost certainly due to the artificial method of preparing them. Similar negative results were found in some experiments by Straumanis * on the measurement of electrode potentials for different planes of single crystals of zinc. It appears likely that only when naturally developed faces are available will such measurements be of value in throwing light on the conditions obtaining in the lattice of the single metal crystal.

The author wishes again to acknowledge his indebtedness to Prof. Owen for his continued help and advice.

Bangor, May 1931.

XLVIII. *Notes on Weber's Law and the Yellow Spot Effect.* *By* R. A. Houstoun, *D.Sc., Lecturer on Physical Optics in the University of Glasgow* †.

§ 1. In former papers ‡ I showed that König and Brodhun's observations on the least perceptible increment in intensity of light could be represented by a probability curve when they were graphed as $I/\Delta I$ against log I. In conjunction with Jas. F. Shearer § I made experiments on the same subject by different methods ; I desire here to give

* 'Nature,' July 13, 1929.
† Communicated by the Author.
‡ Phil. Mag. viii. p. 520 (1929); x. p. 416 (1930).
§ Phil. Mag. x. p. 433 (1930).

an account of further experiments made by means of the fourth apparatus described in the joint paper.

This apparatus consisted of a spectrometer over the collimator lens of which was fitted a Wollaston prism and in front of the telescope of which was mounted a rotating polarizer consisting of two glass plates. The observer saw a double image of the slit the halves of which could be altered in intensity relatively to one another by rotating the polarizer, and the experiment consisted in adjusting the polarizer so that the difference in intensity was just perceptible. The results varied considerably from time to time as in most branches of physiological optics, and I first of all tried to see whether it was possible to obtain greater consistency by changing the method.

Instead of adjusting the polarizer so that the two halves of the image were just perceptibly different I made them equal, going over the whole range of intensity eight times. I thus had eight readings for each intensity. The mean of these was calculated, and then the root mean square of their differences from the mean. When the just perceptible difference is low, the setting to equality is accurate, and I thought that the root mean square might be proportional to the just perceptible increment and at the same time more consistent than the latter. In this I was disappointed. While there is a rough proportionality between the two quantities, it was obvious that the error of observation depended on other factors besides the least perceptible difference, and that its root mean square was no more consistent than the mean of the latter.

I next attempted to use a contrast method. Let us suppose that in fig. 1 abscissæ represent log I and ordinates the sensation of brightness. If we have three unequally bright surfaces such that the contrast between the first and second is equal to the contrast between the second and third the sensations of brightness aroused by these surfaces can be represented respectively by ordinates Aa, Bb, and Cc, such that

$$Bb - Aa = Cc - Bb.$$

Let us raise the intensity of the first surface to B and of the second to C, and seek out a new intensity of the third such that the contrasts are again equal. Then

$$Dd - Cc = Cc - Bb,$$

where Dd represents the sensation aroused by the third surface. By proceeding in this way we can fix a series of

ordinates advancing in arithmetical progression, and by joining the tops of these ordinates the curve can be obtained.

Fig. 2 shows how this method was put into operation. A and B are two 220 volt 100 watt clear gas-filled lamps the intensity of which could be regulated by rheostats. W is a wedge photometer in front of the lower half of which rotated a vertical surface shown by the dotted line. This surface was covered with the same paper as the surfaces of the wedge, and its upper edge was horizontal and sharp. The lamp A was first moved into the position A′ which made the illumination of both faces of the wedge equal. It was then moved

Fig. 1.

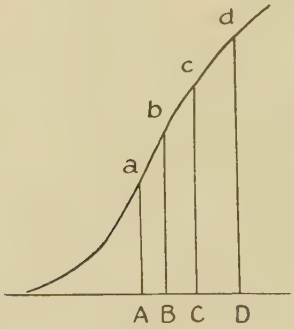
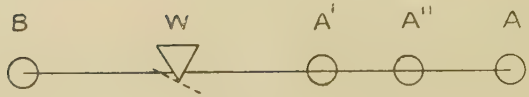


Fig. 2.



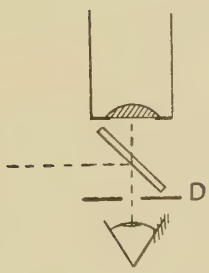
back into the position A, making the right-hand face darker than the left-hand face. The rotating surface was then adjusted until its intensity was intermediate between the two faces of the wedge, and it made the same degree of contrast with each of these faces. The lamp A was next moved up to the position A″, which made the intensity of the right-hand face equal to the intensity of the movable surface. The distances of A, A′, and A″ give the intensities of three surfaces making equal contrast. The current through B was then altered until it gave the same illumination on the left-hand face of the wedge as the other lamp gave on the right-hand face when in position A″, the movable surface adjusted until it had the same intensity as the right-hand face when

illuminated by the other lamp in position A, and the new position of this lamp sought out which gave equal contrast. And so on, until the complete range of intensities was explored.

The results obtained by this method agreed with those given by the method of least perceptible difference, but they were not so accurate. It was also not possible to obtain such high intensities as by the method of least perceptible difference, the maximum in the one case being forty times the maximum in the other. So I reverted to the former arrangement.

A change was, however, made in the method of standardizing the brightness of the field. Previously a piece of clear glass was set at 45° to the axis of the telescope close up to the eye-piece, and by its means the test object and a surface illuminated by a standard lamp were viewed simultaneously. A

Fig. 3.



knowledge was required of the diameter of the pupil of the eye at the time of making the comparison, and the value corresponding to the level of illumination in question was simply taken from Reeves' data. This value has proved to be inaccurate for the conditions in question, and consequently the new procedure indicated in fig. 3 has been adopted. In the figure, D is a diaphragm of diameter 3·25 mm., which is less than the diameter of the pupil of the eye at the intensity in question. Thus the aperture for the comparison surface is fixed beyond doubt.

As a consequence of Reeves' value being unsuitable the values of the logarithm of the intensity given for tables iv. and v. of the former paper* are inaccurate. To correct them 0·43 must be subtracted in each case. The position of the upper curve in fig. 2 of the same paper is also inaccurate ; it

* Phil. Mag. x. p. 436 (1930).

must be displaced 0·43 to the left, which brings the position of its maximum into agreement with the position of the maximum of the lower curve.

After finding that nothing was to be gained by a change of apparatus I proceeded to investigate the effect of colour on the least perceptible difference. According to König and Brodhun $\Delta I/I$ was the same for a given luminosity for all six wave-lengths investigated, except at low intensities when there was a difference between the two ends of the spectrum. I used a 220 volt 40 watt Pearl Osram lamp as source, with Wratten standard tricolour red, green, and blue filters, and made first the right-hand and then the left-hand just appreciably brighter for antilog 3·1, 3·77, and 2·43 I.U., taking at each intensity the colours one after the other, so that any difference in the results would be due to difference in colour and to nothing else. Ten sets of readings were made altogether, and no difference was revealed.

I next studied the effect of dark adaptation. The following table gives some results made with the blue filter at low intensities :—

Table I.

Log I.U.	Light adapted.	After 5 min.	After 25 min.
$\bar{1}$·00	·98	·67	·39
$\bar{1}$·33	·83	·67	·23
$\bar{1}$·67	·70	·29	·23
0·00	·53	·35	·18

The first column gives the logarithm of the intensity in I.U. and the other columns values of $\Delta I/I$ obtained respectively with a light adapted eye, and after 5, and 25 minutes dark adaptation. The change with time is a very marked one. The question arises as to whether the change can be regarded as due to the rods coming into action as a group with their thresholds distributed about a mean. I do not think it possible to learn anything definite on this point from the observations on $\Delta I/I$ themselves, because they are very difficult to make on account of the double variation with intensity and time. We also never know how much oblique fixation is being used in this region.

A series of observations was then made for red over the whole range by nine different observers. Each observer made about ten independent sets of readings—that is, he passed from the low end to the high end of the range or *vice*

versâ ten times, making first the right- and then the left-hand just appreciably brighter at each intensity. In some cases one or two practice sets were made before the observations were entered on; in other cases no practice sets were required. The observer in each case regulated the current, read the scale, and entered up the readings himself by the aid of a flash-lamp. The repetition of these operations keeps the eye in a uniform state of partial light adaptation, which, I think, adds to the consistency of the observations. The observers included one member of the staff, three research students, and five undergraduate honours physics students of the University. The mean results are given in the following table :—

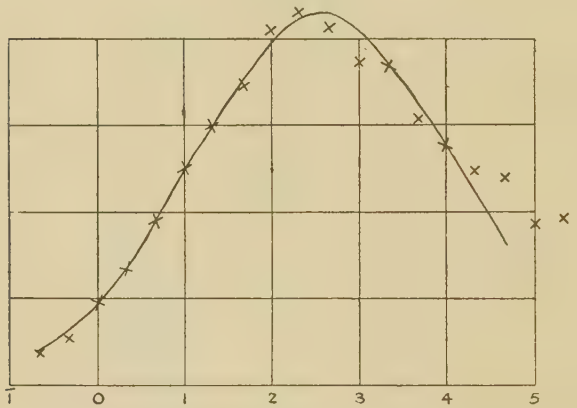
TABLE II.

Log I.U.	1.	2.	3.	4.	5.	6.	7.	8.	9.
$\bar{2}$·67	—	—	—	—	—	—	—	3·4	—
$\bar{1}$·00	—	—	—	—	—	—	—	5·3	—
·33	—	—	2·0	2·2	6·6	3·3	3·1	7·5	—
·67	—	—	3·5	3·4	6·8	8·4	5·0	9·6	3·9
0·00	4·9	5·9	6·3	4·8	20·2	11·4	10·0	13·0	4·6
·33	8·3	10·1	9·2	8·9	21·2	14·8	12·4	16·4	6·7
·67	11·3	13·4	13·8	16·2	34·1	19·2	17·3	21·2	8·5
1·00	16·0	15·2	18·5	22·6	42·7	27·0	22·7	27·7	12·0
·33	18·2	18·8	25·1	30·8	37·6	30·5	30·0	24·7	14·8
·67	19·3	20·7	29·0	34·0	44·0	42·0	34·4	24·7	16·7
2·00	19·8	22·6	35·0	52·4	59·0	57·0	30·7	22·2	21·4
·33	21·5	27·4	40·7	58·7	69·2	41·5	28·3	26·0	23·6
·67	18·8	24·3	52·3	51·5	57·0	29·5	27·8	21·1	30·3
3·00	22·6	22·3	51·1	35·3	40·4	29·6	27·8	19·3	25·5
·33	27·0	28·2	43·5	25·2	42·6	28·1	25·4	18·5	23·9
·67	21·5	23·8	32·7	20·1	46·2	24·2	22·4	15·3	17·0
4·00	22·1	26·4	23·0	16·1	43·6	19·9	18·6	14·4	14·6
·33	23·4	19·2	20·7	12·9	27·3	16·9	16·2	13·8	10·7
·67	19·6	19·0	18·5	11·0	35·8	15·3	15·9	14·6	10·4
5·00	16·2	15·2	16·1	13·6	26·5	11·8	11·5	—	7·9
·33	17·0	15·0	13·8	19·6	21·5	—	10·4	—	7·6

The first column of the table gives the logarithm of the intensity in I.U. (one photon = 10 I.U.) and the other columns the values of $I/\Delta I$ obtained by each of the nine observers. When the values are graphed, some of them are very irregular, and there are great differences in the shape

of the curve from observer to observer. One of the observers, no. 8, differed from the others in being somewhat insensitive to red light and slightly colour blind ; his maximum occurred at a decidedly lower intensity than the maxima of the others. I consequently omitted him in taking the mean of all the observers. This mean was obtained by raising the maximum ordinate in each case to the same value, and then adding the ordinates. The result is shown in fig. 4. The smooth curve is a probability curve fitted to the points by trial and error. Each of the points on the curve is the mean of about eighty determinations. The maximum ordinate of the curve corresponds to a value of $I/\Delta I$ of about 45.

Fig. 4.

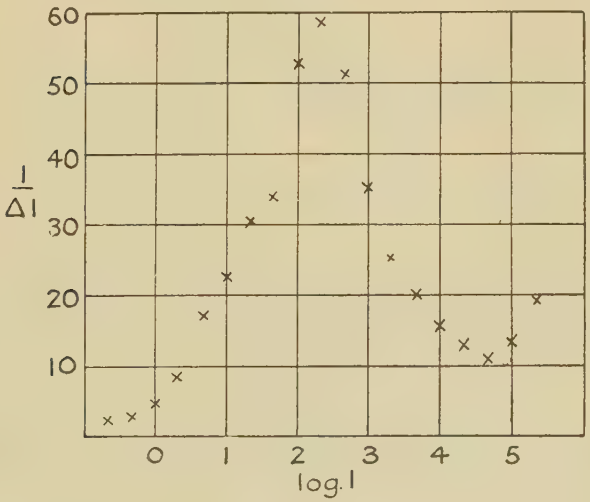


One of the observers, no. 4, obtained a curve of a very peculiar shape. His observations are graphed in fig. 5. The diameter of the eye-ring of the instrument was 2·27 mm., and as I thought he might have an exceptionally narrow pupil at high intensities I got him to make a few additional observations at the highest intensity after his set was completed, and watched his eye from the side through a short-focus telescope. The area on which the light fell was visible by scattered light as a red disk on the surface of the eye. At first the red disk fell inside the pupil, but he immediately jerked the eye up and caught it on the iris. The action was automatic and beyond his control. In taking the mean his last four observations were omitted. The observers were instructed to hold the eye so as to get the image as bright as possible, but it is probable that the want of agreement

between curve and readings at the high end is partly due to all the light not entering the eye. This point would require a special investigation.

The curves of all nine observers were integrated graphically, and are shown in fig. 6. As a consequence of the integration the curves become much more regular. The abscissæ give log I.U. and the ordinates the sensation S on an arbitrary scale. To avoid confusion three of the curves have been drawn two squares too high and four of them one square too high. It will be observed that there is a great difference in the height of the curves, and that some are much straighter than others.

Fig. 5.



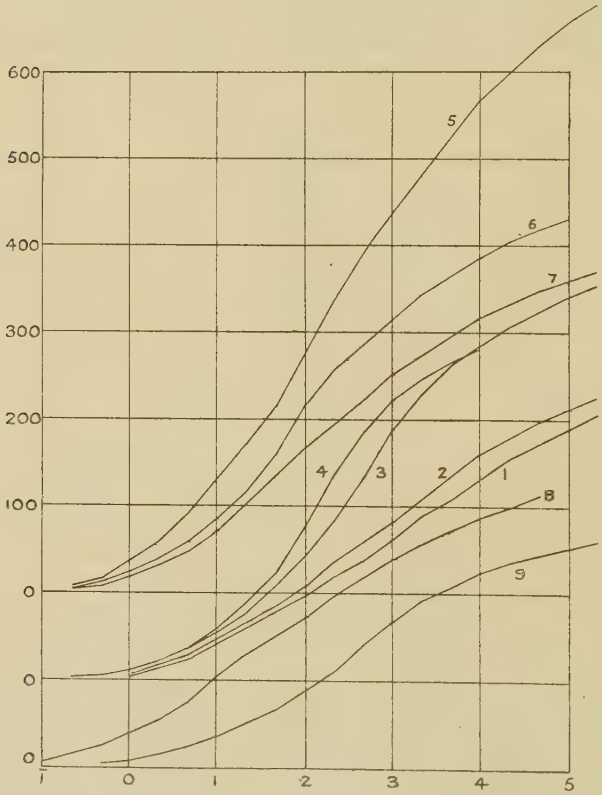
The consistency of König and Brodhun's work is, I think, partly a matter of temperament and partly the result of practice. There is little doubt they must have put in a considerable amount of preliminary training before taking the readings recorded in their papers.

Owing to the diversity in the shapes of the curves it is clear that if a connexion is to be sought between the variation of sensation and of acuity with intensity both sets of readings must be made by the same observer.

§ 2. If a red and a blue light of low intensity are compared by a wedge photometer, the result varies with the distance

of the eye from the photometer. If the eye is near the photometer the ratio of red to blue is greater than when it is far away. The image of the photometer on the retina consists of two rectangles touching each other sharply, and according to Abney, who refers to the effect on several occasions, the latter is due to the fact that in the first case

Fig. 6.



the image falls wholly on the yellow spot and the blue is partially absorbed before reaching the rods and cones, whereas in the second case a large part of the image falls outside the yellow spot. Dow has questioned this explanation*, for the effect is more pronounced when the intensity

* Phil. Mag. xii. p. 121 (1906).

of the image is low, and it is difficult to understand why the fraction absorbed should depend on the intensity of the light.

In order to study the effect I mounted two 20 watt 250 volt Osram colour-sprayed vacuum-lamps on a long photometer bench with a wedge photometer between. One was red and the other was blue. They were rather bright for my purpose when connected directly to the 250 volt lighting circuit, so I joined them in parallel and put them in series with a resistance of about 900 ohms. The candle-power of the red lamp was then 0·041 international candles. The blue lamp was set at a distance of 147 cm. from the wedge, and the red lamp balanced, when the eye was in succession at 20, 40, 80, and 144 cm. from the wedge. The results obtained are shown in the following table:—

TABLE III.

Angle subtended.	Ratio of red to blue.
10° 52′	·379
5° 26′	·486
2° 43′	1·048
1° 31	1·833

The faces of the wedge appeared as a rectangle measuring 5 cm. vertically and 3·8 cm. horizontally, with the line of separation down its middle, and the angle entered above is the angle subtended by the 3·8 cm. side at the eye. It is obvious from the table that the effect is a large one.

The transmission factor of the yellow spot has been measured by Sachs*. Taking the transmission for the Na line as 1·0 he finds the factor to decrease gradually from this value to the end of the spectrum, where it becomes 0·605. Let us suppose that one-half of the area of the largest image above is yellow spot. It is difficult to know what to take for the transmission factor in my experiment, for while the red lamp emits only red, the blue emits much red and green as well as blue. Let us assume 1·0 for the red and an average value of 0·8 for the blue. When the image falls wholly on the yellow spot 0·8 of the blue goes through, but in the case of the largest image, owing to half the light missing the yellow spot, the average factor will be 0·9. Thus in passing from the largest to the smallest image the ratio red to blue is increased in the proportion of 8 to 9, which is much less than

* *Arch. f. d. ges. Physiol*, l. p. 574 (1891).

the observed ratio. The calculation above is somewhat sketchy, but it is nevertheless difficult to escape the conclusion that the yellow spot is not yellow enough to form the basis of an explanation. Besides, Gullstrand is quoted by Parsons* as stating that the yellow coloration is a post-mortem change.

The above readings were made with a dark-adapted eye, an eye in equilibrium with the state of illumination of a room which contained no lights but the rather dim red and blue lamps in question. The following table shows how, for the same position of the lamps and the largest image, the result varies during the process of adaptation :—

Table IV.

Time.	Ratio of red to blue.
0	1·055
20 sec.	·601
2½ min.	·501
16 min.	·408

The first determination recorded was made with a 16 C. P. lamp placed directly behind the wedge, so that the latter just obscured its bulb, the lamp being switched on. For the other determinations I light-adapted the eyes by gazing at this same lamp close up for one minute. It was then switched off, and I waited until the intensity of the blue face of the wedge came up to the level of the red for the position of the red lamp in question.

Dark adaptation for 20 minutes had no effect on the ratio when the photometer was viewed from 144 cm. ; but when viewed obliquely at this distance, 5° to the side of the point of fixation, the ratio became 0·25 after 15 minutes.

The effect is thus closely connected with dark adaptation. If we accept the duplicity theory, and assume that the rods are more sensitive to blue than to red, the results described are due to the image passing from the cones to the rods as it spreads out from the fovea and to the rods coming into action as dark adaptation develops. If we do not wish to commit ourselves to the mechanism of the duplicity theory it is only necessary to assume the existence of two states of the eye, the photopic state and the scotopic state. The eye is more sensitive to blue light in the scotopic state. The fovea is always in the photopic state, and as dark adaptation

* 'Colour Vision,' p. 13.

develops the surrounding region passes from the photopic to the scotopic state. There is no reason to suppose that the coloration of the retina changes in passing from the one state to the other.

Granted that the main effect is due to dark adaptation, the question may be asked as to whether part of it may be due to the coloration of the macula. In order to settle this point observations were made above the level at which dark adaptation sets in. Two 200 C. P. half watt lamps were placed on the bench, and the faces of the wedge illuminated through a Wratten red standard tricolour and a peacock-blue standard complementary filter. The illumination on the faces of the wedge was then about 500 metre-candles. The lamp giving the blue light was kept fixed, and the other lamp set to equality both by Mr. Jas. F. Shearer and myself with the eye at 20 cm. and at 144 cm. from the wedge. We both found that the red became weaker when we moved away from the wedge, Mr. Shearer's value for the ratio being 1·227 to 1 and mine being 1·155 to 1 ; these results are the mean of three determinations in each case. So at very high intensities the eye shows a reversed yellow spot effect. The most natural way of explaining this is to assume that fatigue for red and blue is different in the different parts of the retina. This reversed effect, it will be noticed, is small compared with the direct one.

Clerk Maxwell*, when observing a long slit through a glass prism, noticed a black spot to run up and down the yellow part of the spectrum as he raised and lowered his head. He considered that this was caused by absorption in the yellow spot, but states that the experiment is not easy to perform. It is more probable that the effect was due to the fovea not being in the same state of dark adaptation as the surrounding region. I have tried to repeat the experiment, but was unsuccessful. In the experiments with the wedge photometer the eye averages the intensity over the whole face. It might be expected that in the case of the largest image the surfaces would match at the middle of the line of separation, but be out of balance above and below ; but this is wrong—they match all over at once. It is possible that in Maxwell's experiment the black spot is averaged out in the same way with some observers.

Since the yellow spot effect is due to the passage from the photopic to the scotopic mechanism, it arises from the same cause as the Purkinje effect. In order to exhibit its connexion

* Brit. Assoc. Rep. 1856.

with the latter I measured it for three additional illuminations. In the experiment recorded in Table III. the illumination on the blue face of the wedge was 0·01 metre-candle. I moved the blue lamp in succession into other positions, so that the illuminations on this face were 0·0300, 0·108, and 0·297 metre-candles, and set the red lamp to equality for each of these positions at all four distances of the eye. The values of the illumination given above were calculated from the positions of the blue lamp. If they had been calculated from the positions of the red lamp the results would have been different. Consequently they can only be regarded as giving an idea of the magnitudes involved. The following table gives the results, the former set being included for completeness. Each value is the mean of two determinations.

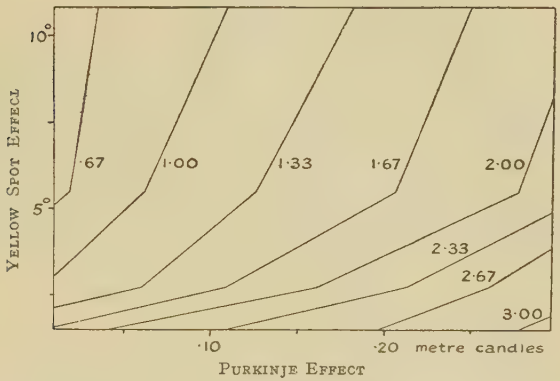
Table V.

Metre-candles.	Angle subtended by short side of rectangle.			
	10° 52′.	5° 26′.	2° 43′.	1° 31′.
·0100	·38	·49	1·05	1·83
·0300	·63	·82	1·10	1·93
·108	1·00	1·23	1.66	2·31
·298	1·88	2·06	2·90	3·03

The values might be plotted as points on a diagram with metre-candles as abscissæ and angles subtended as ordinates; they vary from 3·03 to ·38. It is, however, better to calculate the curves which give the positions for which the ratio has exact values; these curves represent the variation of the ratio, intensity of red lamp to intensity of blue, over the field in the same way as contour lines on a map give the height of a mountain. I have drawn the curves in fig. 7 for values of the ratio advancing in steps of ·33; the positions are of course only approximate, being obtained by interpolation from the table. The figure combines the yellow spot effect and the Purkinje effect on the one diagram. If we confine ourselves to one horizontal, that is, keep the eye at a constant distance from the wedge, and move from right to left, that is, shift the blue lamp away from the photometer, the ratio red to blue diminishes. This is the Purkinje effect. If we confine ourselves to one vertical, that is, keep the position of the blue lamp fixed, and bring the eye nearer the wedge, the ratio red to blue again dimishes. This is the yellow spot effect.

The readings, it should be noted, are for an eye in equilibrium with a dimly illuminated room, and consequently in a high state of dark adaptation. If the eye were light-adapted

Fig. 7.



the value of the ratio would be the same throughout those portions of the diagram in which it is possible to take readings with the eye in this condition.

XLIX. *A Relation between Continued Fractions and Hyperbolic Functions.* *By* H. Ataka (*Meiji College of Technology, Tobata, Japan*)*.

IN dealing with the electrical transmitting networks, both continued fractions and hyperbolic functions are often used. Mr. A. C. Bartlett states in his interesting paper †, recently communicated to this Journal, that the nth power of a second order square matrix is first obtained, and he gives the following theorem :

$$\begin{vmatrix} a, & b \\ c, & d \end{vmatrix}^n = \begin{vmatrix} \dfrac{\cosh(n\theta+\phi)}{\cosh\phi}, & \dfrac{Z\sinh n\theta}{\cosh\phi} \\ \dfrac{\sinh n\theta}{Z\cosh\phi}, & \dfrac{\cosh(n\theta-\phi)}{\cosh\phi} \end{vmatrix},$$

* Communicated by the Author.
† Phil. Mag. p. 735 (October 1930).

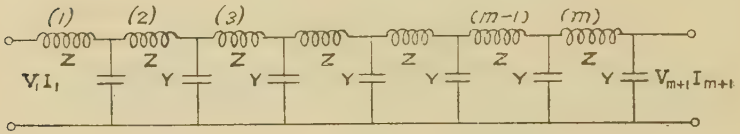
where Z, θ, and ϕ are chosen so that

$$\cosh(\theta+\phi)/\cosh\phi=a,$$
$$Z\sinh\theta/\cosh\phi=b,$$
$$\sinh\theta/Z.\cosh\phi=c,$$
$$\cosh(\theta-\phi)/\cosh\phi=d.$$

We also obtained the same formula about two years ago *. Here we shall note one of the applications of this theorem.

By the aid of this formula we can easily deduce a relation between continued fraction and hyperbolic function. Consider a ladder-shaped transmitting network, of which the series vector impedance is Z and the parallel vector admittance is Y, as shown in the figure. We assume, for the sake of simplicity, that numerically

$$Z=Y=X.$$



Let V_1 and I_1 be the input volt and current, and V_{m+1} and I_{m+1} be the output volt and current. Then we shall have the relation

$$V_1=AV_{m+1}+BI_{m+1},$$
$$I_1=CV_{m+1}+DI_{m+1},$$

where the four constants A, B, C, and D are immediately found by the theory of a passive quadripole or a passive four-terminal network.

$$\begin{vmatrix} A, & B \\ C, & D \end{vmatrix} = \underset{(1)}{\begin{vmatrix} 1 & X \\ 0 & 1 \end{vmatrix}} \cdot \begin{vmatrix} 1 & 0 \\ X & 1 \end{vmatrix} \cdot \underset{(2)}{\begin{vmatrix} 1 & X \\ 0 & 1 \end{vmatrix}} \cdot \cdots\cdots \underset{(m)}{\begin{vmatrix} 1 & X \\ 0 & 1 \end{vmatrix}} \cdot \begin{vmatrix} 1 & 0 \\ X & 1 \end{vmatrix}.$$

This equation can be evaluated by the aid of the function called " Gausssche Klammer Ausdruck."

$$\begin{vmatrix} A, & B \\ C, & D \end{vmatrix} = \begin{vmatrix} [XX\ldots X]_{2m}, & [XX\ldots X]_{2m-1} \\ [XX\ldots X]_{2m-1}, & [XX\ldots X]_{2m-2} \end{vmatrix},$$

where the suffixes denote the number of the letter X in the brackets.

* *Cf.* H. Ataka, Journal of I. E. E. of Japan, p. 843 (August 1928).

On the other hand, we have

$$\begin{vmatrix} A, & B \\ C, & D \end{vmatrix} = \begin{vmatrix} X^2+1, & X \\ X, & 1 \end{vmatrix}^m$$

$$= \begin{vmatrix} \dfrac{\cosh(2m+1)\dfrac{\theta}{2}}{\cosh\dfrac{\theta}{2}}, & \dfrac{\sinh 2m\dfrac{\theta}{2}}{\cosh\dfrac{\theta}{2}} \\ \dfrac{\sinh 2m\dfrac{\theta}{2}}{\cosh\dfrac{\theta}{2}}, & \dfrac{\cosh(2m-1)\dfrac{\theta}{2}}{\cosh\dfrac{\theta}{2}} \end{vmatrix},$$

where

$$\sinh\frac{\theta}{2} = \frac{X}{2}.$$

Thus it follows that

$$[XX\ldots X]_{2m} = \frac{\cosh(2m+1)\dfrac{\theta}{2}}{\cosh\dfrac{\theta}{2}},$$

$$[XX\ldots X]_{2m-1} = \frac{\sinh 2m\dfrac{\theta}{2}}{\cosh\dfrac{\theta}{2}},$$

and also

$$\frac{[XX\ldots X]_{2m-1}}{[XX\ldots X]_{2m}} = \underbrace{\frac{1}{X+}\,\frac{1}{X+}\,\frac{1}{X+}\cdots\cdots\frac{1}{X+}\,\frac{1}{X}}_{\text{to } (2m-1) \text{ stages}}$$

$$= \frac{\sinh 2m\dfrac{\theta}{2}}{\cosh(2m+1)\dfrac{\theta}{2}},$$

$$\frac{[XX\ldots X]_{2m-2}}{[XX\ldots X]_{2m-1}} = \underbrace{\frac{1}{X+}\,\frac{1}{X+}\,\frac{1}{X+}\cdots\cdots\frac{1}{X+}\,\frac{1}{X}}_{\text{to } (2m-2) \text{ stages.}}$$

$$= \frac{\cosh(2m-1)\dfrac{\theta}{2}}{\sin 2m.\dfrac{\theta}{2}}.$$

The last two relations were already pointed out by A. E. Kennelly *.

* A. E. Kennelly, Am. Annals of Mathematics (January 1908).

L. *The Calculation of the Mobility of Monomolecular Ions.* *By* H. R. Hassé, *M.A., D.Sc., and* W. R. Cook, *M.Sc.**

THIS paper is supplementary to two former papers. The first section puts on record the results of the calculation of the integral occurring in the formula for the diffusion of molecules between which the repulsive and attractive forces can be represented by the expressions λr^{-9} and μr^{-5} respectively, r being the distance between the molecules. The theory and the method of calculation are given in the first of the papers referred to above †.

The second section contains the application of this formula to the calculation of the mobilities of mono-molecular ions, and may be regarded as a continuation of the work in the second of the two papers ‡, which may be consulted for further details. This calculation is based on theoretical considerations prior to the advent of the quantum mechanics, and in particular on two assumptions; these are: (i.) that the attractive force between a positive charged particle and a neutral molecule is given by the expression

$$(\mathrm{K}-1)e^2/2\pi \mathrm{N}r^5 \equiv qr^{-5}$$

(using the notation of the paper referred to [L. T. p. 140]), which is given by the classical theory of electrostatics, and (ii.) that in the calculation of the forces between a positive ion and a molecule this attractive force, due to the extra charge on the ion, is to be added to that between the two molecules, and their repulsive force is to remain unaltered. The second assumption is by no means satisfactory, but it is the best that can be made at present; it will be possible to test both assumptions when further progress has been made in the determination of the forces between atoms and ions on the basis of the quantum mechanics §.

The third section deals with a new aspect of the problem of the mobility of ions. Recent experiments have established the existence of a transfer of charge from the ion to the atom by the capture of an electron in an encounter. Though it is not yet possible to deal with the effect of such a transfer on the mobility of the ion in the general

* Communicated by the Authors.

† H. R. Hassé and W. R. Cook, Proc. Roy. Soc. A, cxxv. p. 196 (1929).

‡ H. R. Hassé, Phil. Mag. i. p. 139 (1926). This paper will be cited as Langevin's Theory, or simply L. T.

§ The work of the first two sections of this paper is based on calculations carried out by one of us (W. R. C.) in 1928.

case where the ion and atom are considered as centres of attractive and repulsive forces, it has proved to be a fairly simple matter to modify the calculations in the paper on Langevin's theory so as to include the case of such a transfer. In this theory there is an elastic collision between the atom and ion when their centres are at a definite distance apart, and a certain proportion of these collisions may be assumed to result in a transfer of charge. It is found that in all cases such a transfer results in a decrease in the mobility of the ion, which is quite considerable if there is a transfer of charge at every collision.

1. *Calculation of the Integral.*

The diffusion coefficient D_{12} for the case of molecules of masses m_1 and m_2, whose number per unit volume is n_1 and n_2, is given by Chapman by the formula *

$$D_{12} = \frac{3}{16}\left(\frac{m_1+m_2}{hm_1m_2}\right)^{\frac{1}{2}} \frac{\pi^{\frac{1}{2}}}{(n_1+n_2)P_{12}}(1+\epsilon), \quad . \quad . \quad (1)$$

where $h=(2RT)^{-1}$, R being the gas constant, and

$$P_{12} \equiv 2\pi\left(\frac{m_1+m_2}{hm_1m_2}\right)^3 \int_0^\infty U^5 e^{-U^2} dU \int_0^\infty \cos^2\theta d(p^2), \quad (2)$$

where

$$U^2 = \frac{hm_1m_2}{m_1+m_2} V^2,$$

V is the relative velocity of the molecules before their encounter, p is the perpendicular from one molecule on the path of the other, and $\pi-2\theta$ is the deflexion produced by the encounter. The factor $1+\epsilon$ depends on the masses and concentration of the molecules and on the forces between them.

The detailed discussion of the dynamics of the encounter is given in the paper referred to for the case where the force between the molecules is $\lambda r^{-9}-\mu r^{-5}$, in which the value of

$$\int_0^\infty \cos^2\theta\, d(a^2) \equiv C(k)$$

is calculated, where

$$p^2 = \left(\frac{\lambda'}{V^2}\right)^{\frac{1}{4}} a^2, \qquad \lambda' = \lambda\frac{(m_1+m_2)}{m_1m_2}, \qquad k=(Us)^{-1},$$

and

$$s^2 = (2RT\lambda)/\mu^2.$$

* Chapman, Phil. Trans. A, ccxi. p. 449 (1912).

In order to carry out the integration with respect to U in (2) the tabulation of $C(k)$ as a function of k is replaced by algebraic expressions for various ranges of k as follows:—

$$(0\leq k\leq 1),\ C= 0{\cdot}38080 - 0{\cdot}09773k+0{\cdot}03766k^2 +0{\cdot}04992k^3,$$

$$(1\leq k\leq 2),\ C= 0{\cdot}28899 + 0{\cdot}20608k-0{\cdot}33822k^2 +0{\cdot}25454k^3-0{\cdot}04072k^4,$$

$$(2\leq k\leq 4),\ C=10{\cdot}12448 -15{\cdot}88100k+9{\cdot}35137k^2 -2{\cdot}27785k^3+0{\cdot}19924k^4,$$

$$(4\leq k<\infty),\ C= 0{\cdot}78149k^{\frac{1}{2}}- {\cdot}03353-{\cdot}16822k^{-\frac{1}{2}}.$$

The errors in replacing the tabulated values by these expressions are estimated to be less than 1 in 4700, 1 in 6000, 1 in 1300, and 1 in 1380 respectively for the four ranges of values of k given above.

The results of the calculation of $I(s)$, defined by

$$I(s)=\int_0^\infty z^{\frac{9}{2}}e^{-z^2}\,dz\int_0^\infty \cos^2\theta\,d(a^2), \quad . \quad . \quad (3)$$

are given in Table I., together with those of $I(s)\sqrt{s}$, which is more convenient for use when s is small. The errors in this table consequent on those mentioned above are calculated to be less than 0·0008 for $s=0{\cdot}2$, 0·0004 for $s=0{\cdot}3$, 0·0002 for $s=0{\cdot}4$, and to be less than 0·0001 for $s\geq 0{\cdot}5$.

As $s\to 0$, $I\to\infty$, but $I\sqrt{s}\to 0{\cdot}5194$, while $I(s)$ is, for large values of s, approximately equal to

$$0{\cdot}30623-0{\cdot}05536s^{-1}+0{\cdot}01730s^{-2}+0{\cdot}02263s^{-3}.$$

2. *The Mobility of Monomolecular Ions.*

The mobility k of an ion is given on Langevin's theory by the formula $k=2eh\mathrm{D}_{12}$, where e is the charge on the ion, so that from the preceding equations we have

$$k=\frac{3}{16}\frac{eh}{\pi^{\frac{1}{2}}}\left(\frac{m_1+m_2}{hm_1m_2}\right)^{\frac{3}{4}}\frac{1+\epsilon}{(n_1+n_2)(\lambda')^{\frac{1}{4}}\mathrm{I}(s)}, \quad . \quad . \quad (4)$$

which for monomolecular ions, in which case $m_1=m_2=\mathrm{M}$, reduces to

$$k=\frac{3e}{16}\left(\frac{2}{\pi\mathrm{M}}\right)^{\frac{1}{2}}\frac{1}{(2\mathrm{RT}\lambda)^{\frac{1}{4}}}\frac{1+\epsilon}{(n_1+n_2)\mathrm{I}(s)}, \quad . \quad . \quad (5)$$

since $h=(2\mathrm{RT})^{-1}$ and $\lambda'=2\lambda/\mathrm{M}$.

In the experiments on mobilities the number n_2 of the ions is small compared with the number n_1 of the molecules of the gas, so that $n_1 + n_2$ can be put equal to n_1, which may now be written as N, using the ordinary notation of the theory of gases. Further, in this case we can make use of an expression for the value of $1+\epsilon$ given by Chapman *, which can be shown to lie between 1 and 1·015 when the molecules of the gas are elastic spheres. As this case is

TABLE I.

s.	I(s).	I(s) $\sqrt{s}$.	s.	I(s).
0·05	2·2584	0·5050	1·1	·2866
·10	1·5619	0·4939	1·2	·2848
·15	1·2496	·4840	1·3	·2839
·20	1·0431	·4665	1·4	·2836
·25	0·8634	·4317	1·5	·2836
·30	0·7129	·3905	1·6	·2838
·35	0·5971	·3533	1·7	·2842
·40	0·5121	·3239	1·8	·2846
·45	0·4508	·3024	1·9	·2852
·50	0·4067	·2875	2·0	·2857
·55	·3747	·2779	2·2	·2867
·60	·3515	·2722	2·4	·2878
·65	·3343	·2695	2·6	·2888
·70	·3216	·2691	2·8	·2897
·75	·3121	·2703	3·0	·2905
·80	·3049	·2727	3·2	·2913
·85	·2995	·2761	3·4	·2920
·90	·2953	·2802	3·6	·2927
·95	·2922	·2848	3·8	·2933
1·00	·2898	·2898	4·0	·2938

known to provide the greatest value of $1+\epsilon$, the value of this factor can for the purposes of this paper be taken to be unity.

We are now in a position to extend the calculations of the mobility of an ion given in the paper on Langevin's theory. In that paper (p. 150) it was pointed out that the theory could be improved either by using the attractive and repulsive forces between the molecules, as determined from data supplied by the variation of the viscosity of a gas

* Chapman, Phil. Trans. A, ccxvii. p. 175 (1918).

with temperature, or by employing Sutherland's molecular model in which the repulsive force is concentrated in an elastic sphere of radius s_0. In both cases the calculations are based on the two assumptions stated above in the introduction to this paper.

As a particular example of the calculation of the mobility of a monomolecular ion the molecular forces in the case of hydrogen are given by a repulsive force λr^{-9} and an attractive force μr^{-5}, where $\lambda = 0{\cdot}106 \times 10^{-72}$ and $\mu = 0{\cdot}35 \times 10^{-43}$ *, and the additional attractive force between the ion and the molecule is qr^{-5}, where $q = 3{\cdot}54 \times 10^{-43}$. Hence the total attractive force is μr^{-5}, where μ is now equal to $3{\cdot}89 \times 10^{-43}$, and this value, together with that of λ, is to be substituted in the expression $s = (2\mathrm{RT}\lambda)^{\frac{1}{2}}/\mu$, giving $s = 0{\cdot}235$ at a temperature of 15° C. The corresponding value of $\mathrm{I}(s)$ from Table I. is 0·897, and the mobility at atmospheric pressure is then found from (5) to be 18·3 in cm./sec. per volt/cm.

Similarly for argon we have $\lambda = 1{\cdot}09 \times 10^{-72}$, and $\mu = 3{\cdot}23 \times 10^{-43}$, and further $q = 7{\cdot}48 \times 10^{-43}$, so that the constant for the total attractive force is $10{\cdot}71 \times 10^{-43}$ and a similar procedure leads to the value 2·68 for the mobility.

In the case of helium, which is of interest in view of the experiments of Tyndall and Powell †, the values of the force constants have to be taken from the investigations of Lennard-Jones on the equation of state of a gas ‡. We thus find that $\lambda = 1{\cdot}14 \times 10^{-74}$, $\mu = 0{\cdot}43 \times 10^{-44}$, and q is calculated to be equal to $9{\cdot}34 \times 10^{-44}$, so that the total attractive force constant is $9{\cdot}77 \times 10^{-44}$, whence the mobility of the helium ion calculated from these data is 29·9.

It is pointed out in the paper by the authors from which the data for λ and μ for hydrogen and argon are taken that the values of μ when obtained from viscosity data may differ considerably from those obtained from data given by the equation of state. The differences in the mobilities calculated from the two sets of data are indicated in the table showing the complete results.

If Sutherland's model is used the values of the constants s_0 and μ are taken from viscosity data when applied to this model §, and the mobility is calculated from the formula given in L. T. (pp. 141 and 149). As an example, we have

* Hassé and Cook, *loc. cit.* p. 211.

† A. M. Tyndall and C. F. Powell, Proc. Roy. Soc. A, cxxix. p. 162 (1930).

‡ Lennard-Jones, Proc. Roy. Soc. A, cvii. p. 157 (1925).

§ Hassé and Cook, Phil. Mag. iii. p. 977 (1927).

for argon $s_0 = 1{\cdot}49 \times 10^{-8}$, and $\mu = 1{\cdot}29 \times 10^{-43}$. Since $q = 7{\cdot}48 \times 10^{-43}$, as before, the total attractive force is $8{\cdot}77 \times 10^{-43}$, and the mobility has the value 2·68, which in this case is the same as that obtained by treating the molecule and ion as centres of force. In the case of helium the Sutherland model is not adequate for the representation of the viscosity at low temperatures. It was found, however, that this model could be used in the range from 195° abs. to 373° abs., and gave $s_0 = 1{\cdot}00 \times 10^{-8}$, $\mu = 1{\cdot}11 \times 10^{-44}$, which, with $q = 9{\cdot}34 \times 10^{-44}$, makes the force constant due to the total attractive force equal to $10{\cdot}45 \times 10^{-44}$, and gave a mobility equal to 24·9, which differs somewhat from the value 29·9 obtained above.

Table II. gives the results of calculations of this kind. The first column is taken from the previous paper (L. T. p. 152), in which the molecule is treated as an elastic sphere; in the second column the mobility is determined on the basis of the Sutherland molecular model; and the third column gives the results when the molecule and ion are considered as centres of attractive and repulsive forces. The results are in all cases based on the two assumptions stated at the beginning of this paper.

TABLE II.

Mobility of Monomolecular Ions.

Gas.	Elastic sphere.	Sutherland model.	Centres of force.
Air	3·41	3·13	3·35 (*a*)
Argon	2·95	2·68	2·68 (*a*) 3·13 (*b*)
Helium	26·3	24·9	29·9 (*b*)
Nitrogen	3·44	3·17	3·47 (*a*) 4·05 (*b*)
Hydrogen	19·0	18·2	18·3 (*a*) & (*b*)

(*a*) Data obtained from viscosity.
(*b*) Data obtained from equation of state.

The most interesting feature of the table is the general agreement between values which are determined by different formulæ and are based on data obtained from different sources *.

* This general agreement applies only to the values of the mobility at a definite temperature (15° C.), and it is to be expected that the variation with temperature will be different for the different molecular models, in which case it will be possible to test their suitability by a further comparison with experiment.

The order of magnitude of these values of the mobility calculated for a pure and dry gas is higher than that usually obtained experimentally, but Tyndall and Powell, in the paper referred to above, have shown the marked effect of small traces of impurity on the mobility of the positive ion, and ions of mobility 14 and 17 have been found by them in helium. These values are much closer to the values given in the above table than those obtained in previous experiments.

The same authors have also pointed out the possibility of a transfer of charge by electron capture at collision. The effect of such a transfer of charge on the mobility of the charged ion is dealt with in the following section, in which the problem is treated in the cases (i.) where the molecule or atom is assumed to be an elastic sphere, and (ii.) where the Sutherland molecular model is used. For the reasons stated in the introduction it would be premature to attempt to deal with the more general case of attractive and repulsive centres of force.

3. *Effect of Transfer of Charge at Collision.*

If it is assumed that there is a transfer of charge from an ion I to an atom A when the centres of the ion and atom are at a distance σ from each other, then the atom A becomes the ion I′, and the deflexion produced by the encounter, measured by the angle between the directions of I and I′ at infinity, is now 2θ instead of $\pi-2\theta$. Thus the effect of such a transfer at a collision is to change $\cos^2\theta$ in (2) into $\sin^2\theta$.

We shall assume, to start with, that this transfer occurs at every collision. It is then necessary to separate out the contributions to $\int_0^\infty \cos^2\theta\, d(p^2)$ which arise from deflexions without collision and those that are produced by elastic collision. The tabulated values given in the previous paper (L. T. p. 147) have therefore to be examined afresh from this point of view.

Using the notation of that paper, the mobility depends on a quantity A, defined as 3/16Y, where

$$\mathrm{Y} \equiv \int_0^\infty y e^{-z^2} z^4\, dz, \qquad y \equiv \int_0^\infty \cos^2\theta\, d(\beta^2), \qquad . \quad (6)$$

and β^2 is a variable proportional to p^2 in (2) above.

It is necessary to calculate y as a function of $z\lambda$, where λ is defined in terms of the attractive force between the ion

and atom and the distance σ of nearest approach by the equation

$$\lambda^2 = 8\pi p\sigma^4/(K-1)e^2 \quad . \quad . \quad . \quad . \quad . \quad (7)$$

[L. T. p. 141, eq. (6)], in which p denotes the pressure of the gas, $K-1$ is proportional to the polarizability of the

Table III.

$z\lambda\rightarrow$.	0.	$\frac{1}{16}$.	$\frac{1}{8}$.	$\frac{1}{4}$.	$\frac{1}{3}$.	$\frac{1}{2}$.	$\frac{3}{4}$.	1.
$y_1(\beta<1)$ collision	·44894	·42399	·41324	·39872	·39176	·38176	·37345	·37047
$1-y_1$	·55106	·57601	·58676	·60128	·60824	·61824	·62655	·62953
$y_2(\beta>1)$ no collision	·10366	·10366	·10366	·10366	·10366	·10366	·10366	·10366
y	·65472	·67967	·69042	·70494	·71190	·72190	·73021	·73319

Table IV.

$z\lambda\rightarrow$.	1.	1·0723.	1·1547.	1·2235.	1·3333.	1·4716.	1·6667.	2.
$y_3(\beta<1)$ collision	·37047	·36896	·37050	·37834	·39471	·42356	·46730	·53632
$y_4(\beta>1)$ collision	0·0	·00236	·00655	·00837	·00834	·00548	·00281	·00878
$y_5(\beta>1)$ no collision	·10366	·10195	·09423	·08457	·07243	·05783	·04235	·02597
C	0·0	·00244	·01036	·02209	·04167	·07557	·13333	·25000
y	·73319	·73307	·72754	·71995	·71135	·70439	·70557	·72087

atom, and e is the charge on the ion; and Tables III.–V. give the values of y for particular values of $z\lambda$.

The last row of figures in Table III. is obtained by adding those in the two previous rows, since $y = y_2 + (1-y_1)$, where the second term arises from

$$\int_0^1 \sin^2\theta\, d(\beta^2) = 1 - \int_0^1 \cos^2\theta\, d(\beta^2) = 1 - y_1.$$

It will be noticed that the contribution to the value of y of those ions which suffer no collision is less than $\frac{1}{6}$ of the total value at $z\lambda=0$, and decreases steadily as $z\lambda$ increases until it is less than $\frac{1}{4}\frac{1}{5}\frac{1}{0}$ of the total value at $z\lambda=8$.

For the values of $z\lambda>1$, given in the Tables IV. and V., the total value of y is

$$\int_0^1 \sin^2\theta\, d(\beta^2)+\int_1^B \sin^2\theta\, d(\beta^2)+\int_B^\infty \cos^2\theta\, d(\beta^2),$$

where $B\equiv\frac{1}{2}(\sin\epsilon+\operatorname{cosec}\epsilon)$, and $\operatorname{cosec}\epsilon=z\lambda$, since a collision occurs or not according as $\beta^2<$ or $>B$. Thus the value of y for this range of values of $z\lambda$ is equal to, putting $B-1=C$,

$$(1-y_3)+(C-y_4)+y_5,$$

Table V.

$z\lambda\rightarrow$.	2.	3.	4.	6.	8.
$y_3(\beta<1)$ collision	·53632	·67620	·75378	·83439	·87543
$y_4(\beta>1)$ collision	·00878	·10535	·27046	·68210	1·13702
$y_5(\beta>1)$ no collision	·02597	·00820	·00353	·00106	·00045
C	·25000	·66667	1·12500	2·08333	3·06250
y	·73087	·89332	1·10429	1·56790	2·05050

which can be determined from the values of y_3, y_4, and y_5 given above, and is given in the last row of results in each table.

In order to calculate Y from (6) we replace the tablulated values of y as a function of $z\lambda(\equiv t)$ by the following algebraic expressions :—

$(0<t\leq\frac{1}{4})$, $y=0{\cdot}65472+0{\cdot}10227t^{\frac{1}{2}}-0{\cdot}00364t$,

$(\frac{1}{4}<t\leq 1)$, $y=0{\cdot}67601+0{\cdot}14411t-0{\cdot}12237t^2+0{\cdot}03544t^3$,

$(1\leq t\leq 2)$, $y=0{\cdot}53905+0{\cdot}56581t-0{\cdot}50850t^2+0{\cdot}13683t^3$,

$(2\leq t<\infty)$, $y=\frac{1}{4}t+\dfrac{0{\cdot}40112}{t}+\dfrac{0{\cdot}24548}{t^3}$.

The values of $A=3/(16Y)$ are then given in Table VI., in which it is estimated that there may be errors amounting to 0·0003 for $\lambda=0·5$, 0·0016 for $\lambda=1·0$, 0·0011 for $\lambda=1·4$, 0·0002 for $\lambda=2$, and smaller errors for larger values of λ. These errors arise in replacing the tabulated values of y by the above algebraic expressions.

Since the mobility k of a monomolecular ion is expressed by the formula (L. T. eq. (11))

$$k=A\left[\frac{2}{\rho(K-1)}\right]^{\frac{1}{5}},$$

where ρ is the density of the gas and $K-1$ is proportional to the polarizability of the atom or molecule, it will vary as

Table VI.

λ.	A.	λ.	A.
0·0	·4309	1·2	·3795
0·1	·4069	1·3	·3724
0·2	·3983	1·4	·3642
0·3	·3932	1·5	·3552
0·4	·3897	1·6	·3458
0·5	·3882	1·8	·3262
0·6	·3885	2·0	·3070
0·7	·3899	2·4	·2716
0·8	·3910	2·8	·2409
0·9	·3909	3·2	·2165
1·0	·3890	3·6	·1957
1·1	·3851	4·0	·1782

the value of A. In order therefore to compare the mobility of an ion calculated on the assumption that there is no transfer of charge with that calculated on the assumption that there is a transfer of charge at every collision, it is only necessary to compare the values of A taken from the table in the previous paper [L. T. p. 149] with those given above to see that (for a given λ) it will always be smaller when there is a transfer of charge.

A comparison of the values of A in the two cases shows that for large values of λ the differences are small, and actually the differences tend to zero as λ tends to infinity. Referring to (7) this means that in the extreme case of elastic collisions without any attractive field of the type qr^{-5} the transfer of charge at collision makes no difference

to the mobility, a result which can be verified by direct calculation of

$$\int \cos^2\theta\, d(\beta^2) \quad \text{and} \quad \int \sin^2\theta\, d(\beta^2),$$

which will be found to have the same values in this case. The difference in the values of A for any given value of λ is therefore due to the effect of the attractive force qr^{-5}, and it does not appear to be evident without carrying out the actual calculation that a transfer of charge at a collision is going to reduce the mobility.

As an example of the results of this calculation we may take the case of a helium ion. If the molecular model is an elastic sphere $\lambda=0{\cdot}622$, and the mobility k', assuming a transfer of charge, is found to be 17·4 as compared with the value $k=26{\cdot}3$. Taking the Sutherland model, k' is equal to 16·4 as compared with $k=24{\cdot}9$. Again, the values of k' for nitrogen are 2·23 and 2·11 for these two models as compared with 3·38 and 3·17 respectively for the mobility k on the assumption of no transfer of charge.

If it is assumed that a fraction f of the collisions result in a transfer of charge, it is easily seen that $y(f)$, and hence $\mathrm{Y}(f)$, is a linear function of f. This follows from the fact that β^2 is proportional to p^2, which is a measure of the number of collisions for a given relative velocity. For example, if half the collisions result in a transfer of charge the value of $\mathrm{Y}(\frac{1}{2})$ is the arithmetic mean of Y(0) and Y(1), *i.e.*, $\mathrm{A}(\frac{1}{2})$ is the harmonic mean of A(0) and A(1), and it follows that the values of k' for a 50 per cent. transfer of charge are 21·0 and 19·7 in the case of helium for the two models considered above.

As regards the choice of the value of f, Kallman and Rosen * have given an indication of the method of attack on the problem of the transfer of charge on the basis of the quantum mechanics. Although this requires for an accurate calculation of the probability of a transfer of charge a detailed knowledge of the forces between an atom and an ion, it seems reasonable, since the probability is a periodic function of the distance r between the atom and ion, for a certain range of values of r, and then dies down exponentially to zero, to assume that there is a 50 per cent. transfer of charge for r less than a definite value σ, and no transfer of charge for $r>\sigma$. The mobility has therefore been calculated above for such a case as well as for the case of a transfer of charge at every collision.

* *Zeit. für Phys.* lxi. p. 61 (1930).

As regards the value of σ to be adopted, it is possible to obtain results of a qualitative nature from a consideration of the encounter between an atom and an ion treated according to the principles of quantum mechanics. It seems probable that there will be two types of force between a helium atom and a helium ion of the kind familiar to us in the case of the hydrogen molecule. Leaving out of consideration the attractive force qr^{-5} at large distances, one of these types represents a repulsive force at all other distances, and the other shows the possibility of the formation of a helium molecular ion He_2^+, and gives a repulsive force at smaller distances *. If this is the case, there will be an equal probability of the encounter taking place under either of these two laws of force, which may be said to correspond to elastic collisions at distances apart equal to σ_1 and σ_2 respectively, and the correct value of σ to use in the calculations of this paper will therefore be a mean of σ_1 and σ_2.

Table VII.

Mobility of Monomolecular Ion (Helium).

Transfer of charge at collision.	Elastic sphere model.	Sutherland model.
None.	26·3	24·9
50 per cent.	21·0	19·7
100 per cent.	17·4	16·4

Experimental values :—14 and 17.

In the absence of a quantitative solution of this problem the value of σ has been taken to be that given by the kinetic theory of gases. This appears to be approximately the case if the experimental data given by Kallman and Rosen are used, and it is unnecessary in a provisional calculation of this kind to attempt any more refined treatment.

Table VII. gives the results for helium for comparison with the experimental results so far obtained by Tyndall and Powell.

The existence of two values of the mobility of the helium ion is unexpected, and the need for further experiments

* Weizel and Pestel, *Zeit. für Phys.* lvi. p. 197 (1929). The authors are indebted for this reference to Dr. M. Delbrück, who has pointed out its connexion with this problem, and to whom the statements in this paragraph are due. The theory of the formation of He_2^+ has recently been given by E. Majorana, *N. Cimento*, viii. p. 22 (1931).

with gases in a still purer condition has been emphasized by these authors, particularly with a view to clearing up this point. On the theoretical side it has been shown that the effect of taking into account the transfer of charge at a collision is to reduce the high values of the mobility given in Table II. One may hope that further work in theory and experiment will bring the results into closer agreement.

In dealing with this question of the effect of the transfer of charge on the mobility of an ion the authors wish to acknowledge the help received from discussions of the problem with their colleagues in theoretical and experimental physics.

The University of Bristol.
March 1931.

LI. *On the Torsional Oscillations of Iron Wire.* *By* A. G. Hill, *B.Sc., Research Student, University College, Dundee* *.

IT has been shown by previous research (see Proc. Roy. Soc. Edin. 1911) that the equation $y^n(x+a)=b$ holds for a considerable range where y is the extent of oscillation, x is the number of oscillations, and n, a, and b are constants depending on the metal used and the given or selected conditions. J. B. Ritchie (Proc. Roy. Soc. Edin. 1911), investigating the effects produced by varying conditions on the above constants, found that rotational strain, whether with heated or unheated wire, and extensional strain on unheated wire, had little or no effect on the constants. Further work by G. P. Seaman (Proc. Roy. Soc. Edin. 1912) showed that prolonged repetition of extensional stress had little effect, if any, on magnesium wire, but, when the temperature of the wire was raised, n was found to decrease continuously after a temperature of 350° C. was reached. When the temperature was that of liquid air, the values of the constants were the same as at ordinary temperature.

The present work on Iron Wire was undertaken to find the effect, particularly upon n, of variation of the diameter of the wire. This was done under two conditions: (1) when newly drawn wires were used and (2) after the same wires

* Communicated by Prof. W. Peddie, D.Sc., F.R.S.E.

had been subjected during twenty-four hours to torsional oscillation and varying initial magnitude of oscillation.

Apparatus and Experimental Procedure.

A wooden arm firmly bolted to the wall holds the hollow brass socket of the torsion head, which consists of a heavy brass cone with a central detachable pin-vice. By means of projecting screws the amount of torsion could be regulated. A similar pin-vice clamps the lower end of the wire symmetrically to a heavy cylindrical oscillator to which a thin circular ring, carrying a graduated scale, is attached. By means of a reading telescope, the maximum angular rotations about the axis of the wire could be observed.

The apparatus for prolonged fatigue of the wires is described in detail by J. B. Richie (*loc. cit.*). One end of the wire being clamped rigidly, the other end is subjected to repeated rotations of two-thirds of a complete revolution by means of an electrically-driven pendulum. Each wire was subjected to this action for twenty-four hours. Then the wire was left for some time to eliminate any temporary fatigue.

From one large coil of iron wire originally S.W.G. gauge 16, separate lengths were drawn to gauges ranging from numbers 18 to 30 S.W.G., *i. e.*, of diameters varying from ·035 to ·128 centimetre. These wires, in turn, commencing with the thickest, were clamped to the oscillator and the torsion head, care being taken to have no abnormalities in the portion used. A constant length of wire, 53·175 centimetres from the top pin-vice to the bottom pin-vice, being very carefully measured at different times by means of a straight-edge and another wire.

Three double turns, each of two-thirds of a complete rotation, timed so as to amplify the swing, were given initially to the torsion head in the case of the thicker wires. But latterly, as the duration of the vibration of the thinner wires extended over as much as four hours, attention was directed to obtaining an approximately constant magnitude of the initial swing. In every case the scale readings of the first and successive stationary points were noted by means of a telescope. The diameters of the wires were taken as an average from ten readings. These readings showed variation in the third decimal figure, which is apparently due to irregularities produced by the process of drawing.

Considering the equation, $y^n(x+a)=b$, where y, x, a, and b are as previously described, we see that

$$n \log y + \log(x+a) = \log b.$$

Hence, by choosing for "a" a definite value to fit the results of any one experiment, and plotting values of $\log(x+a)$ horizontally and corresponding values of $\log y$ vertically, the points thus obtained lie on an average on a straight line, in so far as the equation is found to apply, and the tangent of the angle which this line makes with the vertical axis is numerically equal to n.

With the wires in the hard-drawn condition it was found that no single value of "a" would satisfy the *complete* range of oscillation, but that in general two, and sometimes three,

Table I.

Diam.	n.	Average value of n, graph C.
·102	1·1 ·61	·86
·0855	1·1 ·49	·8
·0835	·85 ·28	·6
·066	·95 ·41	·68
052	·67 ·5	·58
·05	·51 ·32	·42
·0437	·44 ·34	·39
·0395	·3 ·26	·28
·037	·12 ·22	·17
·033	·14	·14

values were necessary. Difficulty was occasionally found in selecting the best value of n, considerable deviation being shown in the results. Thus gauge 21 gives values of n varying from 0·79 to 0·86—a variation of 9 per cent. The values of n being found to vary considerably, observations were repeated two or three times so as to obtain a more satisfactory average.

The results showed (Table I.) that, for any single experiment, there was always one value of n for large oscillations and another (smaller) for small oscillations. Both these values increased with increase of diameter, the rate of increase of n for large is greater than for small oscillations.

No definite law being apparent it was decided to investigate the average value of n. The average value of n for large or small oscillations in every one experiment, and the average of these for repeated experiments with the same wire was plotted against the diameter (graph C). This graph shows that n increases with increase in diameter, probably tending towards a limiting maximum value. The curve is symmetrical except for a small part amongst the lowest values of n. The points L and M, corresponding to diameter ·5 mm. and ·52 mm. give the point P as an average.

Thus it appears that the value of "n" increases with increase of diameter at first rapidly, then more slowly, tending apparently to a limiting value. The magnitude of the increase is greater for large than for small oscillations, but is similar.

The parameter "a" increases indefinitely with decrease of diameter

Experimental Series 2.

After being subjected to torsional oscillation of two-thirds of a complete revolution for twenty-four hours, some of the

Table II.

Gauge	20.		21.		22.	
y_0	70·72	50·84	65·05	45·63	112·65	104·26
n	00·2	00·155	00·62	00·55	00·111	00·111
Gauge	23.		24.		26.	
y_0	59·41	50·18	128·62	94·71	99·64	62·03
n	00·28	00·29	00·83	00·66	00·65	00·41

above wires were again experimented with in order to find how "n" varied with the diameter under this condition.

Various discrepancies in the previous results having led to doubts as to whether the magnitude y_0 of the initial oscillations had not some effect on the value of "n," it was decided to test this. Accordingly the wires in series 2 were subjected to oscillations varying in magnitude from one to two complete revolutions, and it was found that in every case except one the greater initial oscillation corresponded to the greater value of "n" (Table II.).

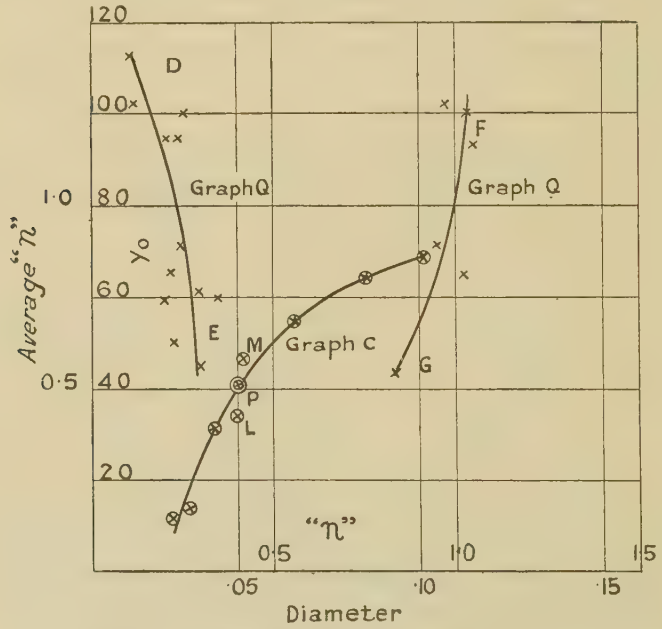
These results are obtained by taking the average of the values of "n" for any one experiment. If, as with gauge 22, the value of "n" for the high initial oscillation is doubtful, the value for a small initial oscillation alone is given. It

will be seen that the results are contrary in the case of the wire gauge 23 alone ; and that the discrepancy in this case is small. The breaking-points, *i. e.*, the points where one value of "n" failed to satisfy the curves, also depended on the magnitude of the initial swings. When the initial swing was increased the breaking-point occurred at a larger angle of oscillation (Table III.).

TABLE III.

Gauge	21.		22.		23.	
y_0	65·05	45·63	112·65	104·26	59·41	50·18
Br.-pt. ...	29·00	28·00	60·00	50·00	33·80	23·20

Gauge	24.		26.	
y_0	128·62	94·71	99·64	62·03
Br.-pt. ...	40·00	31·20	42·00	23·59



The graph illustrating the behaviour of "n" as the diameter and initial swing are varied shows two distinct branches; the upper corresponds to large, the lower to small oscillations, as in series 1. It is very evident that the magnitude of the initial swings had considerable effect on the value of "n." Any effect produced by the twenty-four hours of torsional oscillation would doubtless cause a continuous variation in "n." This effect, however, if present,

is entirely masked by the effect produced by the variation of the initial oscillation.

The values of "n" were then plotted against the initial oscillation (y_0) (see graph Q, p. 570). It must be remembered that the diameter R is also varied in this case. The results show that (1) an increase in y_0 causes an increase in "n," (2) a decrease in R causes a decrease in "n." Hence an increase in y_0, together with a decrease in R, would lead to an increase or decrease in "n," according as the first of the above effects is greater or less than the second.

Graph Q shows (see part DE, graph Q) that in the case of small oscillations an increase in y_0, together with a decrease in R, results in a decrease of "n." For large oscillations (see part GF, graph Q) it appears that an increase is shown, considerable in the case of thick wires and small initial oscillations, but tending to zero as the wires become thinner. Hence, before any definite law can be laid down, further work will be necessary to determine the variation of "n" with y_0 while the diameter remains constant.

We conclude, therefore, that an increase in y_0 causes an increase in "n," this increase being less than that due to change of diameter. If it really is present, any effect produced by the twenty-four hours of torsional oscillation has been masked.

Series 3 deals with the effect of heating the wire to induce softness.

Wire of gauge 19 S.W.G. (diameter ·1020 cm.) was heated to a dull-red heat in a bunsen flame. This softening caused a very considerable increase in "n," the value being:

Large oscillations	(hard)	$n = 1{\cdot}1$
„	„ (soft)	$n = 1{\cdot}7$
Small oscillations	(hard)	$n = {\cdot}61$
„	„ (soft)	$n = 1{\cdot}0$

Summary.

1. An increase in diameter with y_0 fixed causes an increase in "n," this increase diminishing to zero as the diameter increases.

2. An increase in y_0 with diameter fixed causes an increase in "n."

3. An increase in y_0 with diameter fixed causes an elevation of the breaking-point on the curve.

4. An increase in diameter causes a decrease in "*a*." For any one experiment the larger oscillations require the smaller "*a*."

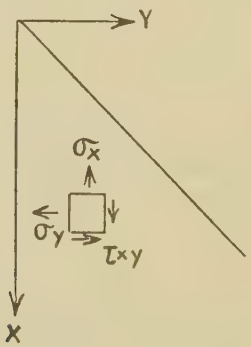
5. Heating the wire to induce softness causes an increase in "*n*."

In conclusion I wish to thank Prof. W. Peddie for his encouraging interest in the subject and guidance throughout, and also Dr. J. Forrest for much helpful advice and frequent suggestions.

LII. *On Two-dimensional Linear Elastic States.* *By* Eugene Kalman, *Visiting Professor of Civil Engineering, California Institute of Technology, Pasadena* *.

IN ordinary engineering practice the validity of the linear distribution of the vertical normal stress in horizontal sections is commonly accepted in the design. In theory

Fig. 1.



matters stand differently. It was shown by Saint-Vénant and Lévy that in two special cases the linear distribution is theoretically valid. In the following the conditions will be set out under which the linear-stress distribution will take place in two-dimensional domains of a general shape.

Assume a system of rectangular coordinates as shown in fig. 1, in which the orientation of the stresses acting on the element $dx\,dy$ is indicated. If the vertical normal stress

* Communicated by the Author.

is linear on all horizontal sections of a given profile, the following relation will hold :

$$\sigma_x(x, y) = y.\mathrm{P}(x) + \mathrm{Q}(x). \quad . \quad . \quad . \quad . \quad (1)$$

The functions $\mathrm{P}(x)$ and $\mathrm{Q}(x)$ may be determined from the conditions of static equilibrium and the equation of compatibility, which are

$$\frac{\partial \sigma_x}{\partial x} + \frac{\partial \tau}{\partial y} + \gamma = 0, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\frac{\partial \sigma_y}{\partial y} + \frac{\partial \tau}{\partial x} = 0, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\frac{\partial^2(\sigma_x + \sigma_y)}{\partial x^2} + \frac{\partial^2(\sigma_x + \sigma_y)}{\partial y^2} = 0 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

respectively, γ being the specific weight of the structure.

Equations (1) and (2) determine the shearing stress if the derivative of σ_x is substituted from (1) into (2), and the expression thus obtained is integrated with respect to y :

$$\tau(x, y) = -\tfrac{1}{2}y^2 \frac{d\mathrm{P}(x)}{dx} - y\frac{d\mathrm{Q}(x)}{dx} - \gamma y - \mathrm{X}(x), \quad . \quad (5)$$

X being an arbitrary function of the variable x only.

Substituting the derivative of this expression into (3) and integrating with respect to y, the stress in the direction of y will be obtained in its general form,

$$\sigma_y(x, y) = \tfrac{1}{6}y^3 \frac{d^2\mathrm{P}(x)}{dx^2} + \tfrac{1}{2}y^2 \frac{d^2\mathrm{Q}(x)}{dx^2} + \frac{d\mathrm{X}(x)}{dx} + \mathrm{X}^*(x), \quad (6)$$

X^* being another arbitrary function of x only.

The values of σ_x and σ_y obtained in this way may be substituted into (4), and the following identity will result :

$$2y\frac{d^2\mathrm{P}(x)}{dx^2} + 2\frac{d^2\mathrm{Q}(x)}{dx^2} + y\frac{d^3\mathrm{X}(x)}{dx^3} + \frac{d^2\mathrm{X}^*(x)}{dx^2} + \tfrac{1}{6}y^3 \frac{d^4\mathrm{P}(x)}{dx^4} + \tfrac{1}{2}y^2 \frac{d^4\mathrm{Q}(x)}{dx^4} \equiv 0. \quad (7)$$

Since this identity must hold for any value of x and y, the four partial relations must be satisfied :

$$\frac{d^4\mathrm{P}(x)}{dx^4} = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$\frac{d^4\mathrm{Q}(x)}{dx^4} = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$2\frac{d^2\mathrm{P}(x)}{dx^2}+\frac{d^3\mathrm{X}(x)}{dx^3}=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$2\frac{d^2\mathrm{Q}(x)}{dx^2}+\frac{d^2\mathrm{X}^*(x)}{dx^2}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

From these expressions the form of P, Q, X, X* may be determined :

$$\mathrm{P}(x) = p_3x^3+p_2x^2+p_1x+p_0, \quad . \quad . \quad . \quad . \quad (12)$$

$$\mathrm{Q}(x) = q_3x^3+q_2x^2+q_1x+q_0, \quad . \quad . \quad . \quad . \quad (13)$$

$$\mathrm{X}(x) = -2p_3x^3-2p_2x^2-2p_1{}^*x-2p_0{}^*, \quad . \quad . \quad (14)$$

$$\mathrm{X}^*(x) = -2q_3x^3-2q_2x^2-2q_1{}^*x-2q_0{}^*, \quad . \quad . \quad (15)$$

the different coefficients p and q being arbitrary constants.

The expressions thus obtained enable us to determine the general structure of the stresses σ_x, σ_y, and τ_{xy} in accordance with the relations (1), (6), and (5) :

$$\sigma_x(x,y) = (p_3x^3+p_2x^2+p_1x+p_0)y + q_3x^3+q_2x^2+q_1x+q_0, \quad . \quad . \quad . \quad (16)$$

$$\sigma_y(x,y) = (p_3x+\tfrac{1}{3}p_2)y^3+(3q_3x+q_2)y^2 - (2p_3x^3+2p_2x^2+2p_1{}^*x+2p_0{}^*)y - (2q_3x^3+2q_2x^2+2q_1{}^*x+2q_0{}^*), \quad (17)$$

$$\tau(x,y) = -(\tfrac{3}{2}p_3x^2+p_2x+\tfrac{1}{2}p_1)y^2 - (3q_3x^2+2q_2x+q_1+\gamma)y+\tfrac{1}{2}p_3x^4 + \tfrac{2}{3}p_2x^3+p_1{}^*x^2+2p_0{}^*x+\mathrm{T}, \quad . \quad . \quad (18)$$

all these quantities being parameters except x and y.

It is seen, therefore, that all two-dimensional elastic states consistent with the postulate of the linear distribution of normal vertical stress along all horizontal sections of the given profile are algebraic functions of the fourth degree in x and y. Hence the number of the possible elastic states is very much limited.

No boundary conditions have been considered as yet. When boundary conditions are prescribed, the parameters in (16), (17), and (18) will be partly or entirely determined, or in some cases over-determined.

The boundary conditions prescribe the normal and tangential load along certain boundary curves. In engineering problems the normal load vanishes on some boundary lines, while the tangential load generally vanishes on the entire boundary.

Denote by α, the inclination of the tangent at any point of the given boundary line, and by σ_n, the prescribed stress acting normally to that tangent at the point under consideration. The tangential load being assumed to be equal to zero, the following relations will hold:

$$\frac{\sigma_x-\sigma_y}{2}\cos 2\alpha - \tau_{xy}\sin 2\alpha = \sigma_n - \frac{\sigma_x+\sigma_y}{2}, \quad . \quad (19)$$

$$\tau_{xy}\cos 2\alpha + \frac{\sigma_x+\sigma_y}{2}\sin 2\alpha = 0. \quad . \quad . \quad . \quad . \quad . \quad (20)$$

From this the values of $\sin 2\alpha$ and $\cos 2\alpha$ may be determined, since the determinant $\left(\frac{\sigma_x-\sigma_y}{2}\right)^2 + \tau_{xy}^2$ can never vanish except for $\sigma_x=\sigma_y$ and $\tau=0$, which is the case of a *régime* of uniform stress like the hydrostatic pressure, in which case, of course, $\sigma_n=\sigma_x=\sigma_y$.

Substituting the values thus obtained for $\sin 2\alpha$ and $\cos 2\alpha$ into the elementary relation

$$\sin^2 2\alpha + \cos^2 2\alpha = 1,$$

the following equation will result:

$$\sigma_x.\sigma_y - \tau_{xy}^2 = \sigma_n(\sigma_x+\sigma_y-\sigma_n). \quad . \quad . \quad . \quad (21)$$

Especially, when both the normal and tangential loads are equal to zero, the well-known relation will hold:

$$\sigma_x.\sigma_y - \tau_{xy}^2 = 0. \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Relations (21) and (22) enable us to solve the problem under consideration in the case of beams and dams.

1. *Rectangular section* (*Beam*).—Along the straight line $y=0$ both $\sigma_n=\sigma_y$ and τ_{xy} are equal to zero (fig. 2). Hence, substituting 0 for y, relations (17) and (18) will furnish

$$p_3 = p_2 = p_1^* = p_0^* = \Gamma = 0,$$
$$q_3 = q_2 = q_1^* = q_0^* = 0.$$

If the dead load of the beam is not considered ($\gamma=0$), the following stress system will result:

$$\left.\begin{aligned} \sigma_x &= (p_1x+p_0)y + q_1x + q_0, \\ \sigma_y &= 0, \\ \tau_{xy} &= -\tfrac{1}{2}p_1y^2 - q_1y. \end{aligned}\right\} \quad . \quad . \quad . \quad (23)$$

Furthermore, no normal load being present at the end section $x=0$, the condition $\sigma_x(0, y)=0$ will hold, that is, in accordance with (23) :

$$p_0 y + q_0 = 0,$$

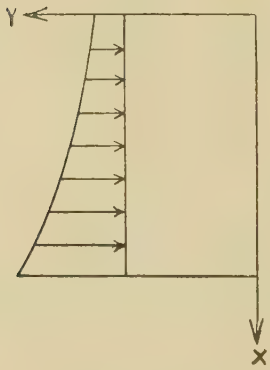
which means

$$p_0 = q_0 = 0,$$

Relations (23) will thus change into

$$\left.\begin{aligned} \sigma_x &= p_1 xy + q_1 x, \\ \sigma_y &= 0, \\ \tau_{xy} &= -\tfrac{1}{2} p_1 y^2 - q_1 y. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (24)$$

Fig. 2.



It is seen that along the loaded face of the beam there is really no load, since $\sigma_y=0$ throughout the whole profile. Besides that, the tangential load being excluded along that face, the following relation will hold, if h be the thickness of the beam :

$$\tau_{xy} = -h(\tfrac{1}{2} p_1 h + q_1) = 0,$$

which means

$$q_1 = -\tfrac{1}{2} p_1 h.$$

The ultimate expression for the stress *régime* will thus be

$$\left.\begin{aligned} \sigma_x &= \tfrac{1}{2} p_1 (2y - h) x, \\ \sigma_y &= 0, \\ \tau_{xy} &= -\tfrac{1}{2} p_1 (y - h) y. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (25)$$

This is the case of a beam loaded by a system of horizontal

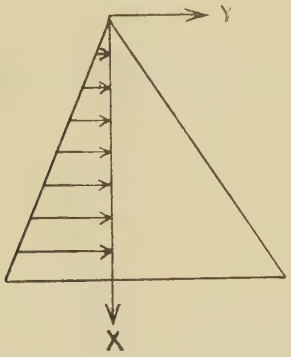
shearing stress acting along the end section of the profile, distributed according to the law

$$\tau = -\tfrac{1}{2}p_1(y-h)h.$$

In other words, this is the case for which Saint-Vénant proved the validity of Navier's hypothesis of the linear distribution of the normal stress on all sections $x=\text{const.}$ The result here obtained shows that this loading is the only one compatible with Navier's hypothesis.

2. *Triangular profile* (*Dam*).—The up-stream face may be assumed as the X-axis (fig. 3). Denote by γ', the specific

Fig. 3.



weight of water. For $y=0$ the conditions must be satisfied:

$$\sigma_y^{\mathrm{g}}(x, 0) = -\gamma' x,$$

$$\tau_{xy}(x, 0) = 0.$$

These two conditions determine the state of stress from (16), (17), and (18):

$$\left.\begin{aligned} \sigma_x &= (p_1 x + p_0)y + q_1 x + q_0, \\ \sigma_y &= -\gamma' x, \\ \tau_{xy} &= -\tfrac{1}{2}p_1 y^2 - (q_1+\gamma)y. \end{aligned}\right\} \quad . \quad . \quad . \quad (26)$$

Now the conditions on the down-stream face must be taken into consideration. According to the foregoing explanations, in this case relation (22) will hold. Put, for instance, $y=Cx$ for the straight line representing the down-stream face, and substitute the expressions (26), transformed

according to $y = Cx$, into relation (22). The following equation will result:

$$\sigma_x . \sigma_y - \tau_{xy}^2 = -\gamma' x[(p_1 x + p_0)Cx + q_1 x + q_0] - [\tfrac{1}{2} p_1 C^2 x^2 - (q_1 + \gamma)Cx]^2 \equiv 0, \quad (27)$$

from which, first of all, will follow

$$\tfrac{1}{2} p_1 C^2 x^2 = 0,$$

which requires $p_1 = 0$, since C cannot be equal to zero because it represents the slope of the down-stream face of the dam. Furthermore, from (27) the following relation will result:

$$-\gamma'(Cp_0 + q_1) - (q_1 + \gamma)^2 C^2 = 0 \quad . \quad . \quad . \quad (28)$$

and

$$-\gamma q_0 x = 0.$$

In applying $p_1 = 0$ and $q_0 = 0$, introducing $C = \tan \alpha$ and eliminating q_1 by the aid of (28), the following elastic state will be obtained:

$$\left.\begin{aligned} \sigma_x &= -(\gamma - \gamma' \operatorname{cotan}^2 \alpha)x + (\gamma - 2\gamma' \operatorname{cotan}^2 \alpha) \operatorname{cotan} \alpha . y, \\ \sigma_y &= -\gamma' x, \\ \tau_{xy} &= -\gamma' \operatorname{cotan}^2 \alpha . y. \end{aligned}\right\} \quad . \quad . \quad . \quad (29)$$

This is exactly the linear elastic *régime* determined by Lévy. While Lévy's investigations showed that the elastic *régime* corresponding to the above boundary conditions is linear, our result shows that Lévy's *régime* is the only one compatible with triangular dam profiles which furnishes vertical normal stress distributed on all horizontal sections according to the linear law.

3. *Trapezoidal profile* (*Dam: water-level at the top*).—This is the type of profile sometimes used in the buttresses of multiple-arch and Ambursen dams. Take again the up-stream face as X-axis. Then the stress system (26) of the preceding case will be obtained. In addition, it is required that no load should act on the upper horizontal boundary line of the profile, which may be chosen as the X-axis (fig. 4). Hence the conditions:

$$\sigma_x(0, y) = \tau_{xy}(0, y) \equiv 0.$$

This means

$$p_0 = q_0 = 0,$$

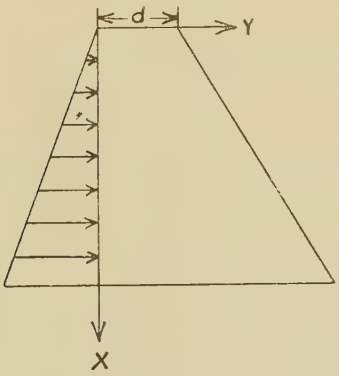
and thus the stress system (26) reduces to

$$\left.\begin{aligned} \sigma_x &= p_1 xy + q_1 x, \\ \sigma_y &= -\gamma' x, \\ \tau_{xy} &= -\tfrac{1}{2} p_1 y^2 - (q+\gamma) y). \end{aligned}\right\} \quad . \quad . \quad . \quad (30)$$

Now the conditions on the down-stream face may be considered. Again relation (22) will be valid ; but, contrarily to the preceding case, the equation of the down-stream face will be of the type $y = Cx + d$. Hence the relation is obtained :

$$-\gamma' x [p_1 x(Cx+d) + q_1 x]$$
$$-[\tfrac{1}{2} p_1 (Cx+d)^2 + (q_1+\gamma)(Cx+d)]^2 = 0,$$

Fig. 4.



from which we have

$$\tfrac{1}{4} p_1^2 C^4 x^4 = 0,$$

and therefore $p_1 = 0$, since C cannot be equal to zero. Furthermore, the other relations will hold :

$$\left.\begin{aligned} -\gamma' q_1 - (\gamma + q_1)^2 C^2 &= 0, \\ 2Cd(\gamma + q_1)^2 &= 0, \\ d^2(\gamma + q_1)^2 &= 0. \end{aligned}\right\} \quad . \quad . \quad . \quad (31)$$

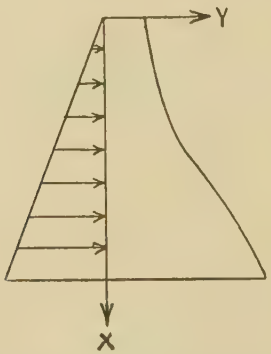
In case $d = 0$ the problem reduces to that treated in (2). Hence d is supposed not to be equal to zero. Consequently the sum $\gamma + q_1$ must vanish. From this the first of the above equations will furnish $\gamma' q_1 = 0$, that is, $q_1 = 0$. However,

according to the second of the above equations (31), this condition means that γ must be equal to zero, which cannot be the case.

It follows therefrom that in the case of trapezoidal profiles the linear distribution of the vertical normal stress along all horizontal sections cannot occur. This result implies that on the horizontal sections the distribution of the shearing stress must be other than parabolic.

4. *Dams with curved down-stream face.*—No load is applied on the top boundary line $x=0$. The up-stream face is assumed as X-axis (fig. 5). According to the preceding example, equations (30) will hold, but with the additional

Fig. 5.



condition $\sigma_x . \sigma_y - \tau^2 = 0$ for the down-stream curve. This condition may be expressed by the aid of (30) as follows:

or $$-\gamma' x(p_1 y + q_1)x = [\tfrac{1}{2}p_1 y^2 - (\gamma + q_1)y]^2$$

$$p_1^2 y^4 - 4p_1(\gamma + q_1)y^3 + (\gamma + q_1)^2 y^2 + \gamma' p_1 x^2 y + \gamma' q_1 x^2 = 0. \quad (32)$$

Hence the down-stream curve must be an algebraic curve of the fourth order, as given by (32). It is seen that the two parameters p_1 and q_1 can be chosen arbitrarily. Equation (32) is quadratic with respect to x, and can be solved without any difficulty. Consequently the curves (32) can be plotted.

Two pairs of values for x and y can be substituted into (32) and the parameters p_1 and q_1 determined. In other words, the down-stream face curve is determined when two arbitrary points, as, for instance, the top and bottom points, are given. Since the curves (32) are of the second order with respect to

x and y, there will be no more than four possible curves passing through the two given points.

For every pair of values (x, y) these curves may be plotted. To any value of x correspond four values of y, and to any value of y two values of x. It is possible that in a certain domain within the top and bottom points all four roots are real, while outside of this domain there are only two real roots. This means that there exist certain points of contraflexure in the curve between the top and bottom points.

5. *General form of dam profiles.*—At the up-stream face the load corresponds to the hydrostatic pressure, which is proportional to the depth. Hence the expression for the normal load $\sigma_n = -\gamma' x$. Denoting the up-stream and down-stream face curves $y_u(x)$ and $y_d(x)$, the following equations will hold:

$$\sigma_x(y_u, x) \cdot \sigma_y(y_u, x) - \tau^2(y_u, x) + \gamma' x \cdot [\sigma_x(y_u, x) + \sigma_y(y_u, x) + x] = 0, \quad (33)$$

$$\sigma_x(y_d, x) \cdot \sigma_y(y_d, x) - \tau^2(y_d, x) = 0. \quad . \quad . \quad . \quad . \quad . \quad (34)$$

Owing to the absence of normal and tangential loads on the top boundary line of the profile, relations (16), (17), and (18) assume the following form :—

$$\left.\begin{aligned} \sigma_x &= (p_3 x^3 + p_2 x^2) y + q_3 x^3 + q_2 x^2 + q_1 x, \\ \sigma_y &= (p_3 x + \tfrac{1}{3} p_2) y^3 + (3 q_3 x + q_2) y^2 \\ &\quad - (2 p_3 x^3 + 2 p_2 x^2 + 2 p_1{}^* x + 2 p_0{}^*) y \\ &\quad - (2 q_3 x^3 + 2 q_2 x^2 + 2 q_1{}^* x + 2 q_0{}^*), \\ \tau_{xy} &= -(\tfrac{3}{2} p_3 x^2 + p_2 x) y^2 - (3 q_3 x^2 + 2 q_2 x) y \\ &\quad + \tfrac{1}{2} p_3 x^4 + \tfrac{2}{3} p_2 x^3 + p_1{}^* x^2 + 2 p_0{}^* x. \end{aligned}\right\} \quad (35)$$

It is seen from relations (33), (34), and (35), that on the up-stream face nine points may be arbitrarily chosen, while on the down-stream face only eight points, owing to the fact that equation (33) is not homogeneous, while equation (34) is homogeneous, and the corresponding pairs of coordinates (x, y) introduced, thus obtaining the necessary number of equations to determine the parameters. Every combination of the parameters will furnish a curve of the 8th order, passing through the given eight or nine points.

It is not possible to state that for a given set of eight or nine points the parameters will be found to be real values.

Furthermore, even by assuming a set of real values for the parameters, curves may result which are not continuous: they may consist of several branches which are wholly independent of each other, each of them passing through a certain group of the given points. And even when the resulting curve is continuous, it may have a shape not acceptable from the technical point of view, inasmuch as it may result not to be monotonous. It is possible that it may have several points of contraflexure both in the horizontal and vertical sense, as shown in fig. 6.

It would be possible to ask for a group of parameters which would furnish the closest possible approximation to the up-stream and down-stream curves of a reasonable dam

Fig. 6.

profile. Denote by $y_u^*(x)$ and $y_d^*(x)$ these reasonable curves. The mathematical problem would be, then,

$$\int_{x=0}^{x_0} \{y_u^*(x) - y_u(x)\}^2 dx = \text{min.},$$

$$\int_{x=0}^{x_0} \{y_d^*(x) - y_d(x)\}^2 dx = \text{min.}$$

Summing up the results obtained in this paper, it is found that for beams and triangular dam profiles the linear states of stress found by Saint-Vénant and Lévy are the only ones consistent with the linear distribution of the stress on all sections parallel to a given direction. In trapezoidal profiles the stress distribution cannot be linear when a full reservoir is considered. As to the preference of horizontal or normal—perpendicular to the bisector—sections in triangular profiles, it is seen from the group of equations (16), (17), and (18) that a convenient choice of the parameters may permit any choice of the direction under consideration. A straight up-stream face is consistent with a well-determined curved

down-stream face which may pass through two points arbitrarily chosen. When both boundaries are curved, eight or nine points may be prescribed on the down-stream or up-stream faces respectively. But the corresponding curves may be imaginary in some part of the domain under consideration, or may not furnish a continuous line passing from the top to the bottom of the profile through the prescribed points. Cases may arise in which the curves are continuous, but are not of a reasonable shape from a technical point of view owing to points of contraflexure, both in the x and y sense. Anyway, only a very limited number of boundary curves are consistent with the postulatum of a linear stray distribution along all sections parallel to a given direction.

LIII. *On the Velocity of Unimolecular Reaction.*

By A. Ganguli, *Benares Hindu University* *.

IN a series of papers †, K. C. Kar and the present author have deduced Langmuir's adsorption equation by Gibbs's statistical method, and have also shown that the same method can be extended to electrical, electronic, and quantaic adsorption. Thus Richardson's thermionic emission formula and Planck's radiation formula have been deduced as special cases of adsorption. In the present investigation the same method will be applied to chemical reactions, and an expression for the velocity coefficient of monomolecular reactions will be deduced from the point of view of adsorption.

Before proceeding to discuss the actual problem, it appears useful to give a brief summary of the existing theories on the subject. Now, one of the most fruitful explanations for the velocity and temperature coefficients of thermal unimolecular reaction is the radiation hypothesis ‡ of Trautz, Perrin, and Lewis. According to this, reactions are brought about by the absorption of radiation (infra-red), the reactant thus becoming activated before undergoing decomposition.

* Communicated by Prof. K. C. Kar.

† Kar and Ganguli, *Phys. Zs.* xxx. p. 918 (1929); *Zs. f. Phys.* lxi. p. 411; lxii. p. 510 (1930); also Ganguli, J. Phys. Chem. xxxiv. p. 665 (1930); *Zs. f. Phys.* lxvi. p. 137 (1930).

‡ Trautz, *Z. Wiss. Photochemie,* iv. p. 160 (1906); W. C. McC. Lewis, J. C. S. (1914–27); J. Perrin, *Ann. Phys.* xi. p. 1 (1919); see also H. S. Harned, J. Frkt. Inst. cxcvi. p. 181 (1923).

Hence it furnishes an extension of Einstein's law of photochemical equivalent to thermal reactions. The theoretical values * for the velocity coefficient obtained by McC. Lewis are, however, at variance from the experimental results, the discrepancy being as high as of the order of 10^7. About the same time, applying a statistical method for the equilibrium constant due to Stern, Herzfeld † obtained the following expression for the velocity of unimolecular reaction :

$$k_0 = \frac{k\mathrm{T}}{h}\left(1 - e^{-\frac{h\nu_{\mathrm{A}}}{k\mathrm{T}}}\right) e^{-\frac{\mathrm{Q}}{\mathrm{RT}}}, \quad . \quad . \quad . \quad . \quad (1)$$

where ν_{A} is the vibrational frequency of the molecule in the crystal lattice. Since for ordinary temperatures ν_{A} is very large, equation (1) reduces to

$$k_0 = \frac{k\mathrm{T}}{h} e^{-\frac{\mathrm{Q}}{\mathrm{RT}}}, \quad . \quad . \quad . \quad . \quad . \quad (1\,a)$$

Q being the heat of reaction, h the Planck's constant of action, and k, R, T having their usual significance. Later on, Dushman ‡ obtained an empirical equation

$$k_0 = \nu e^{-\frac{h\nu}{k\mathrm{T}}} = \frac{\mathrm{Q}}{\mathrm{N}h} e^{-\frac{\mathrm{Q}}{\mathrm{RT}}}, \quad . \quad . \quad . \quad . \quad (2)$$

which agrees with the experimental value of k_0 in several cases. Subsequently, Christiansen § extended Einstein's method of derivation of Planck's law to the reactions, and obtained the following general expression :

$$k_0 = \frac{p_m}{p_n} e^{-\frac{\mathrm{E}_m - \mathrm{E}_n}{\mathrm{RT}}} \cdot \frac{\nu'}{1 - e^{-\frac{h\nu'}{k\mathrm{T}}}}. \quad . \quad . \quad . \quad . \quad (3)$$

If $\frac{p_m}{p_n} = 1$, for small values of $\frac{h\nu'}{k\mathrm{T}}$, equation (3) reduces to Herzfeld's equation (1 *a*) while for large values of $\frac{h\nu'}{k\mathrm{T}}$,

$$k_0 = \nu' . e^{-\frac{\mathrm{E}_m - \mathrm{E}_n}{k\mathrm{T}}} = \nu' e^{-\frac{h\nu}{k\mathrm{T}}}, \quad . \quad . \quad . \quad . \quad (4)$$

which is similar to Dushman's equation (2), the difference being that $\nu' \neq \nu$. Lately S. C. Roy ‖ obtained statistically the following expression for k_0 :

$$k_0 = \frac{8\pi\mu k^2}{h^3} \cdot \frac{\beta_a}{\alpha} \cdot \mathrm{T} \cdot e^{-\frac{\mathrm{Q}_0}{\mathrm{RT}}}, \quad . \quad . \quad . \quad . \quad (5)$$

* W. C. McC. Lewis, Phil Mag. xxxix. p. 26 (1920).
† K. F. Herzfeld, *Ann. Physik.* lix. p. 635 (1919).
‡ S. Dushman, Jour. Am. Chem. Soc. xlii. p. 297 (1920).
§ J. A. Christiansen, *Zs f. Phys. Chem.* civ. p. 91 (1923).
‖ S. C. Roy, Proc. Roy. Soc. A, cx. p. 543 (1926).

where the effective mass $\mu = \frac{m_A \cdot m_B}{m_A + m_B}$, m_A and m_B being the masses of the constituent atoms of the molecule AB undergoing decomposition, $\beta_0 = T.\beta_v$, β_v being the effective area of recombination encounter of the constituent atoms. Very recently Polanyi and Wigner * from probability considerations of the vibrational energy of the molecule deduce the velocity coefficient for a particular axis $\kappa = \nu e^{-\frac{Q}{RT}}$. From three-dimensional considerations

$$k_0 = \frac{2\nu\epsilon}{kT} \cdot e^{-\frac{\epsilon}{kT}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

For low temperature, substituting $\frac{kT}{h}$ for ν in equation (6), we have

$$k_0 = \frac{2\epsilon}{h} e^{-\frac{\epsilon}{kT}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

which is again similar to equation (2).

2. We shall consider that the molecules are at first activated by radiation, and subsequently undergo decomposition according to the following scheme :

$$[AB]_n \longrightarrow [AB]_A \longrightarrow [A] + [B].$$

Thus, if we consider that the molecules can become activated by adsorbing a quantum of frequency ν_0, then since ν_0 is large, the number of activated molecules is given † by the classical form

$$[N_{AB}]_a = [N_{AB}]_n e^{-\frac{h\nu_0}{kT}}. \quad . \quad . \quad . \quad . \quad (8)$$

3. Now we may treat the problem by two different methods. It has been pointed out by Lewis ‡, as well as by Dushman §, that unimolecular reactions resemble thermionic emission (*e. g.*, dissociation of stellar elements according to

* Polanyi and Wigner, *Zs. f. Phys. Chem.* cxxxix. p. 439 (1930).

† The actual expression, according to Bose-Einstein statistics, is

$$[N_{AB}]_a = [N_{AB}] \frac{1}{e^{\frac{h\nu}{kT}} - 1}.$$

‡ W. C. Mc. Lewis and McKeown, J. A. C. S. xliii. p. 1208 (1921).

§ Dushman, Taylor's 'A Treatise on Physical Chemistry,' ii. p. 1051.

Saha *). In a previous paper † it was shown that the number of electrons crossing per unit surface of the metal

$$n=\frac{2\pi mk^2T^2}{Bh^3}e^{-\frac{Q}{RT}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

In the present case, we may postulate that only those (active) molecules which leave the crystalline surface undergo decomposition. Hence the velocity of the reaction may be identified with the rate of emission of the activated molecules. Again, since we are considering here a diatomic molecule (AB), we have to take into consideration the effective mass $\mu=\frac{m_A \cdot m_B}{m_A+m_B}$ instead of m, for the statistical distribution of the molecules in the phase space, thus we have

$$n_{[AB]a}=\frac{2\pi\mu k^2T^2}{Bh^3}e^{-\frac{Q_0}{RT}}, \quad . \quad . \quad . \quad . \quad (10)$$

where Q_0 may be regarded as the heat of dissociation or the adsorption potential. Again, introducing the "effective area" β_v of S. C. Roy, which is in this case the available area through which the molecules escape, we have for the number of molecules escaping per second

$$n'_{[AB]a}=\frac{2\pi\mu k^2T^2}{h^3}\cdot\frac{\beta_v}{B}e^{-\frac{Q_0}{RT}}. \quad . \quad . \quad . \quad (11)$$

Since equation (12) is valid for unit concentration of the active molecules, we have for the total number of molecules leaving the crystal surface per unit time, from (8) and (11)

$$\frac{d}{dt}[N_{AB}]_n=[N_{AB}]_n\cdot\frac{2\pi\mu k^2T^2}{h^3}\cdot\frac{\beta_v}{B}\cdot e^{-\frac{h\nu_0+Q_0/N}{RT}} \quad . \quad . \quad (12)$$

Hence

$$k_0=\frac{1}{[N_{AB}]_n}\cdot\frac{d}{dt}[N_{AB}]_n=\frac{2\pi\mu k^2T^2}{h^3}\frac{\beta_v}{B}e^{-\frac{h(\nu_0+\nu')}{kT}}, \text{ where } Q_0=Nh\nu'$$

$$=\frac{2\pi\mu k^2}{h^3}\frac{\beta_0}{B}\cdot Te^{-\frac{h\nu_{AB}}{kT}}, \text{ where } \beta_0=T\beta_v$$

$$=\frac{2\pi\mu k^2T^2}{h^3}\cdot\frac{\beta_0}{B}\cdot Te^{-\frac{Q_{AB}}{RT}}, \ Q_{AB} \text{ being the total heat of reaction.}$$

$$. \quad . \quad . \quad (13)$$

The expression (13) differs from Roy's equation (4) by the

* M. N. Saha, Phil. Mag. (6) xl. p. 473 (1920).
† Kar and Ganguli, *Zs. f. Phys.* lxii. p. 510 (1930).

factor 4. The statistical weight-factor B corresponds to 'a' in equation (4). It is, however, dimensionally correct. $\frac{\beta_0}{B}$ can be calculated by S. C. Roy's method (*loc. cit.*).

It may be pointed out that the frequency ν_{AB} being the sum of ν_0 and ν' is only an arbitrary virtual frequency, and hence it will be futile to look for the absorption band in the molecule, of the frequency ν_{AB}. Thus Langmuir's criticism* of the radiation theory as regards this point is untenable. In those cases where $Q_0=0$, *i. e.*, the critical increment consists entirely of the radiation energy, the rate of reaction is directly proportional to the number of active molecules. Thus we have from equation (8),

$$k_0=\sqrt{\frac{kT}{2\pi\mu}}\cdot e^{-\frac{h\nu_0}{kT}}. \quad . \quad . \quad . \quad . \quad (14)$$

4. Instead of regarding the reaction as analogous to thermal ionization, we assume that the activated molecules, which are present initially in the chemically adsorbed state in the crystal lattice, leave the surface, and the rate of escape from the surface will correspond to the reaction velocity. We have then, according to Langmuir's theory,

$$c=\frac{k\eta}{1-\eta\beta}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where the Langmuir-Kar-Ganguli constant †

$$k=\frac{(2\pi mkT)^{\frac{1}{2}}}{h}e^{-\frac{a}{kT}},$$

a being the heat of adsorption (adsorption potential). Now, if for the present we neglect β, as being too small, the number of molecules per unit volume,

$$n=k\eta=\frac{(2\pi mkT)^{\frac{1}{2}}}{h}\cdot e^{-\frac{a}{kT}}\cdot\eta. \quad . \quad . \quad . \quad (16)$$

Hence the number of molecules, moving on the axis perpendicular to the surface, that leave unit surface per second

$$n_1=n\cdot\sqrt{\frac{kT}{2\pi m}}=\frac{kT}{h}\cdot e^{-\frac{a}{kT}}\cdot\eta. \quad . \quad . \quad . \quad (17)$$

Now η represents the number of activated molecules as given

* I. Langmuir, J. A. C. S. xlii. p. 2190 (1920).
† Kar and Ganguli, *Phys. Zeits.* xxx. p. 918 (1930).

by equation (8). Thus combining equations (8) and (17) we have as in (14),

$$k_1=\frac{k\mathrm{T}}{h}e^{-\frac{h\nu_{\mathrm{AB}}}{k\mathrm{T}}}=\frac{k\mathrm{T}}{h}.e^{-\frac{\mathrm{Q}_{\mathrm{AB}}}{\mathrm{RT}}}. \quad . \quad . \quad . \quad (18)$$

ν_{AB} being as before the sum of ν_0 and ν', where $h\nu'=a$. It is evident that equation (18) is identical with Herzfeld's equation (1 *a*). As has been pointed out in a previous paper *, we can put $h\nu=k\mathrm{T}$ for ordinary temperature, where ν is the vibrational frequency of the molecule. Thus we have for ordinary and high temperatures

$$k_1=\nu e^{-\frac{h\nu_{\mathrm{AB}}}{k\mathrm{T}}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

which again resembles Dushman and Christiansen's equations (2) and (4).

Now instead of confining ourselves to the number of molecules escaping in one direction, we may very well consider that it may do so in all the three directions corresponding to the space-coordinates. Thus, introducing the three-dimensional correction factor of Polanyi and Wigner in equation (19), we obtain their equation (6)

$$k_0=\frac{2\dot{\mathrm{Q}}}{\mathrm{N}h}e^{-\frac{\mathrm{Q}}{\mathrm{RT}}}, \quad . \quad . \quad . \quad . \quad . \quad (20)$$

which is valid for any temperatures. It may be pointed out that we obtain Dushman's expression with a factor 2 for high temperature, whereas Polanyi and Wigner obtain the the same only for low temperature. Since Dushman obtains confirmation of his empirical equation for thermal reactions at high temperature, our mode of obtaining the same without any special assumption seems to be more justified. It may be further pointed out that the assumption $h\nu=k\mathrm{T}$, as was made in equation (19), which leads to the values of ν of the order of 10^{13} to 10^{15} for ordinary and high temperature, is justified; since the above value of ν is in accordance with the experimental results obtained by Polanyi and Wigner (*loc. cit.*).

Note added in proof.—The values of "k," calculated from equation (13) for several unimolecular reactions, are in good agreement with those obtained experimentally by Hinshelwood, Ramsperger, and other standard authors. The values of $\frac{\beta_0}{\mathrm{B}}$, as extrapolated with the help of the above equation, in

* Ganguli, *Zs. f. Phys.* lxiv. p. 81 (1930).

a good many cases, are of the order of 10^{-15}, thus corresponding to the magnitude of the molecular area. The concept of unimolecular reaction has been extended to the Raman effect as well, and an expression for the intensity of the Raman lines has thereby been obtained. These will be communicated shortly.

In conclusion, I have much pleasure in thanking Dr. K. C. Kar for his interest in this work.

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Benares.
December 1930.

LIV. *The Motion of a Sphere through a Viscous Liquid.* *By* C. E. Lemin, *B.Sc., Andrew Simons Research Scholar at the University College of the South West, Exeter* *.

Introduction.

THE velocity V of a small spherical body moving with uniform velocity through a viscous liquid is given by

$$V = \frac{2r^2(\rho - \sigma)g}{9\eta},$$

where r is the radius of the sphere, ρ and σ are the densities of the sphere and liquid respectively, g is the acceleration due to gravity, and η is the viscosity coefficient of the liquid.

In utilizing this equation for the determination of η, the following conditions are assumed to hold:—

(1) The velocity of fall is so small that higher powers of it may be neglected.

(2) There is no slip between the liquid and the surface of the sphere.

(3) The liquid is infinite in extent.

With reference to condition (1), Rayleigh †, by a comparison of the rates at which the terms included and those neglected in Stokes's equation tend to decrease, has concluded

* Communicated by Prof. F. H. Newman, D.Sc., A.R.C.S., F.Inst.P.
† Phil. Mag. xxxvi. p. 354 (1893).

that the velocity is small when $R \equiv \frac{r\sigma v}{\eta} < 1$. The value of r for which $V = \frac{\eta}{\sigma r}$ is called the critical radius, r_c say. Ladenburg * assumed that the upper limit of r for which the simple formula might be used was of the order $\frac{r_c}{10}$; Zeleny postulated a value $\frac{r_c}{\sqrt{10}}$; whilst Arnold † found, after exhaustive experimental investigation, that there was no deviation from Stokes's law (greater than the experimental error of about 1 per cent.) when $r < 0{\cdot}6r_c$.

As regards the second condition above, there is considerable experimental evidence which shows that, in the case of liquids and solids, no slip occurs. Ladenburg used spheres whose surfaces were corroded, and found that the fall velocity did not differ from that obtained when the spheres were polished. Arnold investigated the problem from the point of view of the coefficient of sliding friction β. Including this, Stokes's formula becomes

$$V = \frac{2gr^2(\rho - \sigma)}{9\eta}\left[1 + \frac{\eta}{\beta r + 2\eta}\right],$$

which reduces to the original form when β is equal to infinity, and to a value 50 per cent. higher if $\beta = 0$.

This correction factor should, however, become appreciable if β has a finite value, even though the latter be large, for a sphere of sufficiently small radius in a liquid of high viscosity. Arnold found that in no case was there any tendency for the value of η, determined by the falling sphere method, to fall below that obtained by Poiseuille's method. He concluded from this that the factor $1 + \frac{\eta}{\beta r + 2\eta}$ could not differ from unity by more than the errors of observation, and deduced the lower limits of β for colza oil and castor oil, for which $\beta \not< 5000$ and 50,000 respectively. This assumes, however, that the value obtained for η by Poiseuille's method is the correct value. But the question of slip enters into Poiseuille's method, as well as in the falling-sphere method, hence it seems doubtful if the above values for β are accurate. According to the kinetic theory of fluids, β should be finite.

* *Ann. d. Phys.* xxii. p. 287 (1907).
† Phil. Mag. xxii. p. 755 (1911).

In practice there is considerable uncertainty as to the actual value of β which should be used in any particular case, and it is quite probable that for sufficiently minute spheres this factor would become of importance.

The third condition obviously cannot be satisfied experimentally. Also early attempts to verify Stokes's formula by Schöttner *, Jones †, and Allen ‡, showed that the walls of the containing vessel exerted a very marked disturbing influence.

Theoretical and practical investigation of this problem was carried out by Ladenburg §. For an infinitely long cylinder and a sphere falling along its axis, he showed that the resistance to the motion was increased in the ratio $1 : \left(1 + 2{\cdot}4\,\frac{r}{\mathrm{R}}\right)$, where R is the radius of the vessel. Hence the formula for the viscosity becomes

$$\eta = \frac{2r^2(\rho - \sigma)g}{9\mathrm{V}\left(1 + 2{\cdot}4\,\frac{r}{\mathrm{R}}\right)}.$$

When Ladenburg tested this formula experimentally, the distance through which the time of fall was measured amounted to only one-half of the total length of the tube. In spite of this, the ends were still found to have a disturbing effect, and, therefore, to eliminate this he introduced a second correcting factor, theoretically deduced, the corrected formula becoming

$$\eta = \frac{2r^2(\rho - \sigma)g}{9\mathrm{V}\left(1 + 2{\cdot}4\,\frac{r}{\mathrm{R}}\right)\left(1 + 3{\cdot}3\,\frac{r}{h}\right)},$$

where h is the total height of the liquid used. He tested this formula, using a filtered solution of Venetian turpentine consisting of three parts resin and one part turpentine, which had a high value of the viscosity coefficient. Constant values of η were obtained by means of this formula.

Arnold, using spheres of wax and rose metal, found that the formula held equally well for liquids of very much lower viscosities, *e. g.*, colza oil ($\eta = 0{\cdot}693$ poise), transformer oil ($\eta = 0{\cdot}070$ poise), and alcohol and water mixture ($\eta = 0\ 019$

* *Ber. d. Wien. Akad.* lxxix. (2) p. 477 (1879).
† Phil. Mag. xxxvii. p. 451 (1894).
‡ *Ibid.* l. p. 323 (1900).
§ *Loc cit.* and *Ann. d. Phys.* xxiii. p. 447 (1907).

poise) provided $\frac{r}{R} < \frac{1}{10}$, this condition being obtained by plotting the viscosity as a function of the sphere radius and making the value of $\frac{r}{R}$ at which the graph departs from a straight line. Some of the spheres used by him were pitted, especially those composed of rose metal, also the wax spheres used were of small density, consequently the term $(\rho - \sigma)$ was only 0·113, and a variation of 0·1 per cent. in density would make a difference of 1 per cent. in result.

The following investigation was undertaken to test the validity of Ladenburg's modification for various values of the ratio $\frac{r}{R}$.

Experimental.

From the observed times of fall of spheres of equal diameter, falling in tubes of varying diameters, η_S the value of the viscosity calculated from Stokes' formula, and η_L that deduced by Ladenburg's modification, were determined. These values were plotted as functions of the fall-tube radius, and the value of $\frac{r}{R}$ for which Ladenburg's modification breaks down is shown by the departure from a horizontal straight line of the graph η_L against R.

The spheres first used were of rose metal, obtained by the same method as that described by Arnold, and varying in radius from 0·03 cm. to 0·08 cm. The results for η obtained with these were not consistent among themselves however, probably due to a slight departure from true sphericity, so it was decided to ensure that the spheres were as exact as possible by using the smallest obtainable steel ball bearings. The use of these also ensured that the density term $(\rho - \sigma)$ was fairly large. These spheres were 0·0625 inch in diameter, guaranteed correct both as to sphericity and size to one part in ten thousand. The diameter was checked by means of a travelling microscope in each case. The density ρ was obtained by weighing a known number and calculating their volume from the value of the radius used. This gave $\rho = 7{\cdot}761$.

To comply with condition (1) one must ensure small velocities, hence it was necessary to use a liquid with a fairly high viscosity coefficient. Glycerine was chosen, the velocity

of fall being then well below the critical value ; but as glycerine is very hygroscopic, and as there is an extremely rapid drop in viscosity with increasing water content, great care had to be taken to keep the sample isolated from water in any form. The density σ of the glycerine at 12° C. was measured before the investigation was commenced, and again at the same temperature after it was finished. The first value of σ was 1·2598, whilst that obtained after the investigation was $\sigma = 1{\cdot}2600$. Hence it is obvious that the composition of the glycerine remained constant during the experiments.

Nine glass fall tubes were used, the internal radii of which varied from 0·280 cm. to 4·840 cm. The liquid column was about 30 cm. in height, and the distance through which the sphere was timed was 15 cm. Three fine file-lines were scratched at right angles to the axis of the tube and 5 cm. apart to denote this distance, so that by timing the fall over the first 10 cm. with one sphere, and the last 10 cm. with another, the uniformity of velocity before entering the measured distance could be ensured. The tubes were mounted vertically, and in order that each sphere might enter the liquid with the minimum of disturbance, and also at the axis of the tube, it was allowed to slide down the side of a piece of glass tubing about 0·3 cm. in diameter, passed centrally through a cork, and extending for about a distance of 2 cm. into the glycerine. A drop of glycerine was allowed to pass through the small tubing before the experiment began, so as to wet the walls. Under these conditions the sphere was found to slide down smoothly and enter the liquid quietly, quite free from air-bubbles, as required.

To avoid rapid fluctuations of temperature in the liquid the latter was surrounded by a large water-bath, and to ensure that there was no temperature gradient set up in the glycerine all measurements were taken at air-temperature. The air-temperature varied throughout the day, but within the space of time necessary for the fall of five spheres (approximately one hour) the variation recorded by the thermometer was only about 0·2° C. Hence the mean time of fall calculated from these five results was taken to represent the time of fall at the mean temperature. The values of η_S and η_L were deduced for this temperature T, and plotted against T. About ten such points were obtained and plotted within a range of approximately 3° C. Within this small range it was assumed that η varied linearly with T, and the most suitable straight line was found by the method of least squares and drawn. By interpolation, therefore, values of

η_S and η_L could be read off for any desired temperature within the range used. Such graphs were obtained for each of the nine tubes used, and the values of η_S and η_L at 12° C. were read off and plotted as functions of the tube radius.

At the commencement of the investigation a sphere was allowed to fall about once every two or three minutes ; but the times of fall were found to decrease gradually instead of remaining constant. The time of fall of the first sphere in a tube of radius 2·35 cm. was 42 seconds, after which there was a gradual decrease to 36·8 seconds for the twentieth sphere, the temperature remaining constant at 11·1° C. After a break of 15 minutes the time of fall was found to have increased again, although not to its original value—the latter

Table I.

Radius of tube=2·35 cm.			Radius of tube=1·425 cm.			Radius of tube=0·860 cm.		
Values of			Values of			Values of		
Temp. °C.	η_S poises.	η_L poises.	Temp. °C.	η_S poises.	η_L poises.	Temp. C.	η_S poises.	η_L poises.
11·13	22·1	20·2	11·20	23·1	20·2	11·39	24·2	19·6
11·51	21·1	19·3	11·51	22·3	19·5	11·45	24·2	19·6
11·87	20·2	18·5	11·83	21·5	18·8	11·79	23·2	18·8
12·09	20·0	18·4	12·10	20·9	18·3	12·00	22·4	18·2
12·42	19·4	17·8	12·26	20·6	18·0	12·31	21·3	17·3
12·70	18·7	17·2	12·61	19·2	16·8	12·72	21·0	17·0
13·09	18·1	16·6	12·73	19·2	16·8	13·08	20·4	16·5
13·28	17·7	16·3	13·10	18·5	16·2	13·19	20·2	16·4
13·51	16·9	15·7	13·34	17·8	15·8	13·50	19·3	15·7
			13·66	17·6	15·5			

being attained after an hour's wait, however. It was assumed from this that the falling spheres had set up currents in the glycerine which made the times of fall, after the first, unreliable for the purpose required. Consequently it was found necessary to allow a certain period of time to elapse between consecutive falls in order that the liquid could settle to a stationary state. A period of 10 minutes was eventually used, and this was found to eliminate the inconsistency.

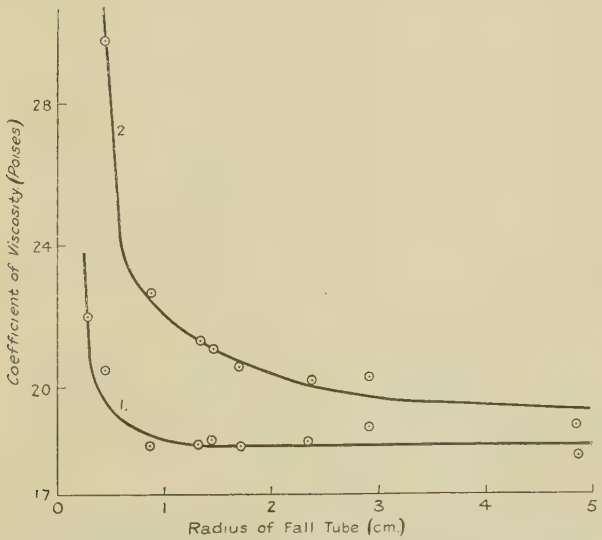
Table I. shows the results obtained with tubes of radius 2·35 cm., 1·425 cm., and 0·860 cm., these being typical, also, of the results obtained with the other tubes.

The values obtained for η_S and η_L at 12° C. with the different fall tubes are given in Table II.

The curves obtained when these values are plotted are shown in the figure, graph (1) being that of η_L against R. It

TABLE II.

R cm.	η_S poises.	η_L poises.
4·84	19·0	18·1
2·90	20·3	18·9
2·35	20·2	18·5
1·70	20·6	18·4
1·425	21·1	18·5
1·302	21·3	18·4
0·860	22·7	18·4
0·435	29·8	20·5
0·280	37·3	22·0



Values of η for different radii of fall tube.

can be seen from this that Ladenburg's modification holds down to a certain value of R, there being a large increase in

η_L with decrease in R below this value. The value of R at which the graph departs from the straight line is approximately 1·25 cm. This gives a value of $\frac{r}{R} = 0{\cdot}06$. The mean of the values obtained on the horizontal part of the curve gives a value for the viscosity coefficient of glycerine at 12° C. of 18·5 poises, which agrees with that obtained by other investigators *.

My thanks are due to Prof. F. H. Newman and Mr. V. H. L. Searle for help and interest in these experiments.

LV. *The Surface Tension of Liquid Metals.*—Part IV. *The Surface Tension of Mercury.* *By* L. L. Bircumshaw, *M.A.*, *D.Sc.*† (*From the National Physical Laboratory.*)

DURING some attempts to measure by the bubble-pressure method the surface tension of certain lead-tin alloys, very great difficulties were encountered in obtaining reproducible values at low temperatures (350°–250°). In some cases a faint film of oxide was visible on the metal after an experiment, but it might be imagined that this would not interfere to any extent, as the bubble is formed underneath the surface of the metal. Another possibility is that the erratic results are due so some disturbance—at the lower temperatures—of the associative equilibrium in the freshly formed surface. In order to obtain further information on this point it was decided to make some experiments on a metal where the formation of a film of oxide of finite thickness would be extremely unlikely. Gold would have been a suitable metal, but it is rather outside the temperature range of the apparatus used for this work. It was therefore decided to use mercury, and measurements of the surface tension of this element, which does not hitherto appear to have been studied below 0°, have been obtained down to −37° (M.P. −38·6).

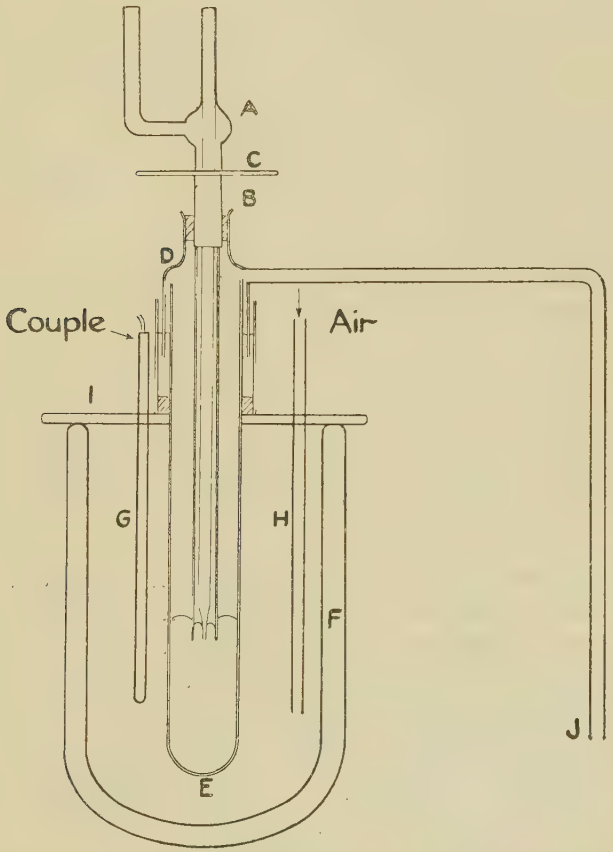
Experimental.

The method used was that previously described ‡. It consisted in the measurement of the pressure required to detach

* Kaye and Laby, p. 30.
† Communicated by Sir J. E. Petavel, K.B.E., D.Sc., F.R.S.
‡ Phil. Mag. ii. p. 341 (1926).

a bubble from each of two tubes arranged concentrically and immersed to the same depth in the metal. The apparatus is shown in fig. 1. The two tubes, sealed together at A, fit tightly into the brass collar B, which carries the circular plate C. The collar is held in position in the mercury seal D

Fig. 1.



by means of a rubber ring. The seal surrounds the silica container E, which is immersed in a large Dewar flask F. G is a thin glass tube containing the thermo-couple, and H a narrow tube through which dry air is blown to stir the freezing mixture in F. I is a light boxwood cover. The tube J acts as an outlet for the gas, and attached to it at J is a considerable length of quill tubing. The ends of the

silica tubes were ground so that the plane of cross-section was parallel to the brass plate C; therefore by levelling the plate the ends of the tubes were in a horizontal plane. The mercury was purified by the method previously given *, and the hydrogen used for blowing the bubbles was freed from oxygen and dried by the method described †. The apparatus was assembled and dry gas passed through the metal for at least two hours. To obtain the low temperature readings the Dewar flask was nearly filled with acetone, and solid carbon dioxide added through a small stoppered hole (not shown in figure) in I. It was found that any temperature down to the freezing-point of mercury could be maintained for any length of time in this manner. The thermocouple used was iron-constantan, and it was calibrated by means of a large volume of water at 20° C., melting ice, and the freezing-point of mercury (−38·6° C.).

With this arrangement the tubes employed in the previous work were first used, and the following result was obtained (P measured in centimetres of water) :—

P (wide).	P (narrow).	a^2.	γ dynes/cm.
21·3	23·75	0·07193	478

This is in good agreement with the value previously obtained, 481 dynes/cm. These tubes were unfortunately broken, and most of the present work was done with tubes which had the following dimensions :—

Mean external diameter of outer tube ...	0·995 cm.
Mean internal diameter of outer tube ...	0·848 ,,
Mean external diameter of inner tube ...	0·100 ,,

The diameter of the container was 2·85 cm. and the zero of the manometer was 0·5 cm.

At 20° the following result was obtained :—

P (wide).	P (narrow).	a^2.	γ dynes/cm.
14·45	27·5	0·07226	480

In the first paper of this series a method was given for the calculation of the correction to be applied for the alteration of the head of metal in the container when a bubble is blown from the outer tube. This has now been modified in the following manner. The depression of the mercury in

* Bircumshaw, Phil. Mag. vi. p. 510 (1928).
† Bircumshaw, Journ. Chem. Soc. 1931, p. 2213.

the wide tube h_0 is first calculated. From the value of r/a for the tube the value of the r/b is obtained from the table

TABLE I.

Temp.	Time.	P wide.	P narrow.	a^2.	γ dynes/cm.
20°	0	14·45	27·5	0·07226	480
	5	,,	27·5	0·07226	480
	15	,,	27·35	0·07158	476
	30	,,	27·25	0·07114	473
10°	0	14·35	27·5	0·07254	483
	5	,,	27·4	0·07209	480
	15	,,	27·15	0·07098	472
	30	,,	27·1	0·07055	470
0°	0	14·15	27·35	0·07258	484
	5	,,	27·25	0·07212	481
	15	,,	26·85	0·07037	469
	30	,,	26·75	0·06994	466
−10°	0	13·95	27·25	0·07290	487
	5	,,	27·2	0·07267	485
	15	,,	26·7	0·07047	471
	30	,,	26·1	0·06786	453
−20°	0	13·7	27·1	0·07302	488
	5	,,	27·1	0·07302	488
	15	,,	26·5	0·07036	471
	30	,,	26·1	0·06863	459
−30°	0	13·4	26·05	0·07345	492
	5	,,	26·95	0·07345	492
	15	,,	26·45	0·07121	478
	30	,,	26·05	0·06950	466
−34°	0	13·35	27·0	0·07387	496
	5	,,	26·9	0·07341	492
	15	,,	26·5	0·07161	480
	30	,,	26·0	0·06946	466
−37°	0	13·1	26·65	0·07324	492
	5	,,	26·6	0·07301	490
	15	,,	25·9	0·06995	470
	30	,,	25·6	0·06865	461

given by Sugden, whence b is calculated, and from the relation $bh_0=a^2$, h_0 is obtained. This method neglects the angle of contact. Let

t=the actual head of mercury in the container.

Δt=the increase in head when a bubble is liberated from the outer tube (due to the volume of metal expelled from the tube and the volume occupied by the bubble).

h_0=the depression of the mercury level in the outer tube.

A=cross-sectional area of the annulus between the container and the outer tube.

a=cross-sectional inside area of the outer tube.

V=Maximum volume of the bubble (taken as a hemisphere).

Then when a bubble is blown from the outer tube we have

$$\Delta t.\mathrm{A} = (t-h_0)a + \mathrm{V}$$

and

$$t+\Delta t = \frac{(t-h_0)a+\mathrm{V}+\mathrm{A}t}{\mathrm{A}},$$

whence $t+\Delta t$ being known, t and hence Δt is easily calculated.

In the previous work (*loc. cit.*) experiments were made to determine the alteration in the surface tension, if any, when the bubble was held for various times on the end of the inner tube at a pressure just below that at which it becomes detached. Normally 40–60 secs. was taken to form and detach the bubble. With silica tubes practically no difference from the normal reading was observed when the time was as long as 30 minutes. In the present work this effect has been investigated at all the temperatures.

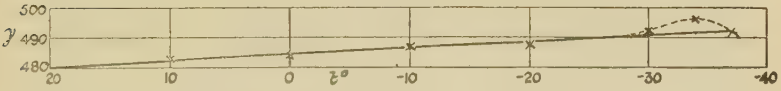
It was found that at room temperature the apparatus could be assembled day after day, and the results very rarely differed by more than 0·5 per cent. Below $-30{\cdot}0°$, however, more difficulty was encountered in obtaining satisfactory duplicate readings; nevertheless with a certain amount of trouble these could be obtained. The difficulties met with in the case of this metal were very much less than those encountered with tin and lead at temperatures near their freezing-points.

Discussion.

The results for the various temperatures are shown graphically in fig. 2, and the points lie well in a straight line.

It will be seen, however, that a relatively marked deviation from a linear relation appears to exist at the lower temperatures. This deviation is small, and is, in fact, very little more than the experimental error; nevertheless, in view of the closeness with which the other points lie on a straight line, it may be regarded as some evidence that the surface tension of mercury falls slightly just before the freezing-point is reached. This behaviour has already been noticed in

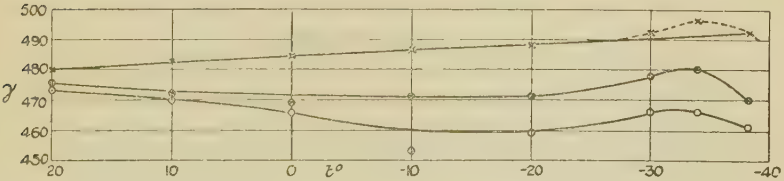
Fig. 2.



cadmium * and copper †, but would, of course, in the present case (mercury) require considerable confirmation. The curve through these points is shown with a dotted line.

In fig. 3 are given the values obtained after hanging the bubble on the end of the tube for 15 and 30 minutes respectively. The normal values, given when the time taken to form and detach the bubble was 40–60 secs., are plotted for comparison. Owing to the difficulty of maintaining the bubble in this position for longer than a few minutes, no great reliance can be placed on these figures, but it will be seen that in both cases the results are lower than the normal

Fig. 3.



readings, and that this lowering increases with the time of hanging, and becomes considerably greater at the lower temperatures. An interesting point is that both these curves pass through a maximum at about −32·0°. The cause of this lowering of the surface tension is somewhat obscure. It is unlikely to be due to the time required for the establishment of an associative equilibrium in the newly

* Bircumshaw, Phil. Mag. iii. p. 1286 (1927).
† Drath and Sauerwald, *Zeit. Anory. Chem.* clxii. p. 301 (1927).

formed surface, as the available evidence for this, in the case of pure liquids, shows that it is complete in a very short time —fraction of a second *. There is still the possibility that in these cases (present work) it is due to the slow adsorption at the mercury-gas interface of some impurity contained in the mercury or the gas, or from the silica tube ; but in view of the extensive precautions taken to clean the tube and purify the hydrogen and mercury this explanation may be considered unlikely.

Summary.

The surface tension of mercury has been determined by the method of maximum bubble pressure from 20° down to −37·0° (freezing-point −38·6°). Some evidence has been obtained that the surface tension passes through a maximum at (approximately) 33°. When the bubble is held for a certain time at the end of the tube at a pressure just below that necessary to detach it, *i. e.*, when the surface is formed some time before a determination is made, a small decrease is observed in the surface tension, this fall increasing considerably at the lower temperatures.

30th April, 1931.

LVI. *Observations on Mr. Narliker's Paper on the Significance of Bode's Law.*

To the Editors of the Philosophical Magazine.

Gentlemen,—

In his introduction to Mr. Narliker's paper † Sir Joseph Larmor points out that since the paper was written the recent work of M. Pierucci has come under their notice and that their attention has now been directed to an earlier discussion by Miss Blagg. Sir Joseph concludes by mentioning the possibility of Bode's Law being abandoned. In this connexion an alternative, which I proposed in 1919 ‡, may be worth consideration.

* Lenard, *Ann. der Physik*, xxx. p. 209 (1887); Schmidt and Steyer, *Ann. der Physik*, lxxix. p. 442 (1926).

† *Suprà*, p. 67.

‡ 'The Observatory,' no. 545, November 1919, p. 402.

The times of orbital revolution of the planets are approximately in the ratio of the cubes of simple integers. It follows from Kepler's third law that the major axes of the orbits of the planets are approximately in the ratio of the squares of simple integers. These laws apply not only to the sun and planets but also to systems of satellites.

I have less hesitation in drawing attention to this in view of the fact that this law of planetary distances was rediscovered in 1929 by Professor Caswell *, who stated that so far as he was aware the relation had not hitherto been reported.

Yours faithfully,

A. F. Dufton.

Greenbank, Garston, Hertfordshire.
13th July, 1931.

LVII. *The Magnetic Field of a Circular Cylindrical Coil.*

To the Editors of the Philosophical Magazine.

Gentlemen,—

In the Phil. Mag. for April this year (No. 72) Professor H. B. Dwight discusses the problem of Magnetic Field of a Circular Cylindrical Coil. May I draw Professor Dwight's attention to a discussion of a rather similar problem by myself published in the 'Proceedings of the Royal Society,' vol. lxiv. (1898)? In this paper Professor Dwight will find a table of the numerical values of the derivatives of the first seven Zonal Harmonics which may be useful to him.

Yours faithfully,

C. Coleridge Farr.

Canterbury College, University of N.Z.,
Christchurch, New Zealand.
28th May, 1931.

* 'Science,' April 5, 1929.

LVIII. *Notices respecting New Books.*

Natural Trigonometric Functions. By Howard C. Ives, C.E. (John Wiley & Sons, Incor., New York. Chapman & Hall, Ltd., 11 Henrietta St., Covent Garden, London, W.C. 2. Price 45*s.* net.)

NUMEROUS tables of sines, cosines, tangents, and cotangents have been published to seven places of decimals for intervals of one minute of angle. The intervals in this collection have been reduced to ten seconds, sines and cosines to seven places, tangents and cotangents to eight significant figures with first differences. Multiples of first differences are provided where the entries can be linearly interpolated. Multiples of differences of six digits are of little value. For cotangents of small angles, it would have been advantageous to give the series development of this function and tables of coefficients for second and third differences. Shorter tables for the conversion of angles into radian measure, radii from arc and chord definitions, tangent and external distances and long chord of a one degree curve, with a chapter explaining their use, follow the main table. A considerable part of one table gives the definitions of sine, cosine, etc., formulæ for the solution of triangles, right-angled triangles included, and other elementary parts of trigonometry. Much care has been taken with the printing and general arrangement and in checking the entries of the tables. The price of the book, however, compares unfavourably with that of Andoyer's fine fifteen figure tables of these functions.

Applied Mathematics for Engineers. Vol. III. By T. Hodgson, B.A., B.Sc. (Chapman & Hall, Ltd., 11 Henrietta Street, London, W.C. 2. Price 13*s.* 6*d.* net.)

The third and last volume of Mr. Hodgson's work on applied mathematics introduces the study of differential equations of general use in the solution of engineering problems. Partial differentiation and double and triple integration, supplementing the ground covered in the second volume, ordinary differential equations including equations with constant coefficients, simultaneous linear equations and partial differential equations are given clear and adequate treatment, with chapters on elementary Fourier analysis and spherical trigonometry. The applications to mechanical and electrical problems include the bending of beams and struts, the whirling of shafts, thermodynamics, with particular reference to the properties of steam and the application of vectors

to alternating currents. The extensive provision of exercises was a valuable feature of the two earlier volumes: in this volume, problems on the subject matter are set at the end of each chapter, a considerable number on integration and the solution of various types of equations. Mr. Hodgson's book will be invaluable to engineering students and to those entering upon the study of harmonic analysis and differential equations.

Magnetic Phenomena. By S. R. Williams, Ph.D., D.Sc. (McGraw-Hill Publishing Co. Ltd., 6–8 Bouverie Street, London, E.C. 4. Price 15*s.*)

This book by Prof. Williams, the latest addition to the International Series in Physics, though described as an elementary treatise on magnetic phenomena, gives a comprehensive account of the growth and development of this science, especially the advances made during the present century. The wide scope of the subject and the fact that the book runs only to some two hundred pages, make it impossible to describe these topics in detail. Even with these limitations, the author has made a general survey of this field of physics, the study of which should arouse the interest of ts readers in the many research problems, theoretical and experimental, awaiting solution; researches in magnetic susceptibility, magnetostriction, magnetic properties of crystals, the Zeeman effect and its bearing on atomic structure. Theories of magnetism and magnetic models are briefly dealt with in the final chapters. In the bibliography and the foot-notes numerous references will be found to the more important memoirs, not least, the author's own contributions to magnetic theory.

Deux heures de Physique.—II. Structure de l'électricité. By F. Wolfers. Editions Kra. (20 Rue Henri-Regnault. 20. Paris. Price 20 francs.)

Of the three volumes which have appeared in the Collection Fontenelle, two deal with various aspects of modern physics, one on electrostatics by M. M. Biquard and Joliot, and the other, a clear and concise account of some of the recent work in electricity and magnetism by Dr. Wolfers. The author gives a historical review of the developments in the study of the structure of matter and electricity, which can be read with pleasure and profit by those interested in the progress of physical science.

Brief supplementary notes on the mass-spectrograph, the Bohr atom and Rydberg's constant, electron charge and mass and other topics are given in the appendices, and a short bibliography of recent works on the kinetic theory of gases, thermodynamics, radioactivity, and atomic structure.

The Universe in the Light of Modern Physics. By Max Planck. Translated by W. H. Johnston. (London: George Allen and Unwin, 1931. 4*s.* 6*d.*)

The present work is a translation of two books: *Das Weltbild der neuen Physik* and *Physikalische Gesetzlichkeit im Lichte neuerer Forschung*, lately published in Leipzig. It is a masterly survey, on general lines, of the present position in physics. It is beautifully written and delightfully free from vague speculations and irrelevant ideas. It will give pleasure to the expert and the amateur alike.

Les Ultra Sons et la Biologie. By F. Wolfers. (Albert Blanchard, Paris, 1931. 9 francs.)

This small pamphlet is the fourth issued in the new *Collection de Suggestions Scientifiques*, published in Paris under the direction of Professor Léon Brillouin. In his editorial introduction, Brillouin remarks that practically all the ideas upon which science has been built up appeared when first formulated to be fantastic, arbitrary, and even absurd; that indeed some of those which have influenced science most profoundly have been relegated, at the outset, to the category "des élucubrations fantaisistes et absurdes." He recalls, too, the notorious case of Carnot, whose notes on the principle of equivalence were lost and found by chance long after, when they had only a historic interest.

The idea of this series is to provide opportunities for the publication of ideas, even if they appear to the majority of contemporary scientists as fantastic and unconventional. As the editor points out, no fantasy of the scientific mind can rival nature herself "si curieuse, si variée, si inimaginable."

Professor Wolfers puts together in this tract his ideas as to the rôle which is played in biological science by the *ultra-sons* which have been rendered accessible in experiments of Langevin. He refers to the well-known results of Wood and Loomis, who have studied the effect of these sound waves on the red corpuscles of the blood and on microscopic organisms; to the less well-known idea of Brillouin who forsees the possibility of a kind of "phonotherapy" of the future, capable (who knows?) of treating such disorders as sciatica, gout, and rheumatism. Various ideas are advanced as to animals reputed to be dumb, which, in fact, may emit these ultra sound waves; these waves, it is thought, may be useful in explaining the well-known facts that certain organisms are able to communicate with each other at a distance, and the many curious facts of sexual attraction.

Those who are interested in speculations and in novel conceptions, those who are ever searching for new ideas, should make a point of seeing this pamphlet and the others to be published in this study.

LIX. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 408.]

June 3ed, 1931.—Prof. E. J. Garwood, M.A., Sc.D., F.R.S., President, in the Chair.

THE following communications were read:—

1. 'A Contribution to the Petrology of the Metamorphic Rocks of East Greenland.' By John Dugdale Holt Wiseman, B.A.

This paper deals with the petrology and genesis of the metamorphic rocks of East Greenland collected by the Cambridge Expedition of 1929 between latitudes 72° and 74° N.

Regionally metamorphosed igneous and sedimentary rocks are the characteristic rock types from both the Central Metamorphic Complex and the Musk-ox Fjord Inlier; unmetamorphosed igneous rocks are rare. The Franz Josef Beds are structurally above the Central Metamorphic Complex. Separating the Franz Josef Beds from that Complex is a thrust with a zone of sheared rocks exhibiting magnificent cataclastic structures. The Franz Josef Beds are metamorphosed for some little distance above the thrust, and the metamorphism appears to have taken place prior to the thrusting.

Backlund has postulated that the metamorphic rocks of the Musk-ox Fjord Inlier and the Central Metamorphic Complex originated through the magmatization of the lower Franz Josef Beds, but this hypothesis receives little support, either microscopically or chemically, from the present investigation. Their genesis may probably be explained by the regional metamorphism of igneous and sedimentary rocks.

A series of rocks from west of Deceit Bay, Kempe Fjord, illustrates the gradual production of gneissic banding with increasing granulitization.

Some evidence is presented which assigns a Pre-Cambrian age to the metamorphism of the Central Metamorphic Complex and the Musk-ox Fjord Inlier.

2. 'The Geological Work of the Cambridge Expedition to East Greenland in 1929'. By Mark Mervyn Leofric Parkinson, B.A., and Walter Frederick Whittard, Ph.D., D.I.C., A.R.C.S., F.G.S.

In East Greenland all systems are represented except the Silurian and the younger Tertiary.

The Expedition was mainly concerned with the rocks underlying the Old Red Sandstone, and particularly with their tectonics. A Jurassic succession was determined, however, at Antarctic Harbour and Lower Callovian ammonites obtained.

The Old Red Sandstone rests with marked unconformity upon the Franz Josef Beds. The ancient landscape has been laid bare locally, and there is evidence that pre-existing valleys have been re-excavated by the modern drainage.

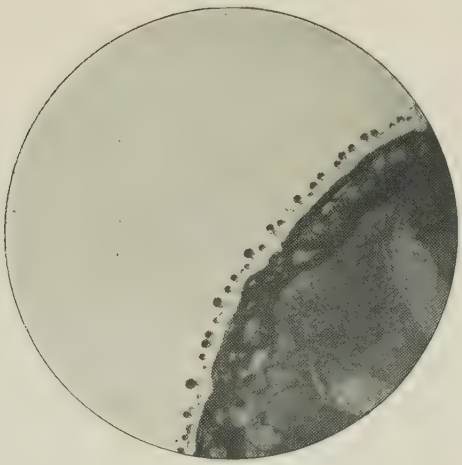
The Franz Josef Beds, ranging in age from Pre-Cambrian to Lower Ordovician, comprise a thick series of sediments exhibiting great lithological variety. Dr. Poulsen has obtained fossils characteristic of the Lower Cambrian, Upper Ozarkian, Upper Canadian, and (?) Lower Ordovician.

The Petermann Series, referable to the lowest Franz Josef Beds, is separated on the east from the main outcrop of the Franz Josef Beds by the Central Metamorphic Complex, and is limited on the west by the Western Metamorphic Complex. The Musk-ox Fjord Inlier is difficult to correlate and receives separate treatment; it is composed of Metamorphic Complex bounded by Franz Josef Beds. Evidence is produced in support of a Pre-Cambrian age for the Metamorphic Complexes.

Progressing inland from the East Greenland coast, three belts of sediments referable to the Franz Josef Beds alternate with three belts of Metamorphic Complex. The tectonics of the main outcrop of the Franz Josef Beds were examined in greatest detail; at the base, a zone of shearing approximately 1000 feet thick is developed, and consists mainly of granulitized and mylonitized representatives of the underlying Central Metamorphic Complex. Towards the north of the examined outcrop at Junction Valley, the zone of shearing, delimited by thrusts of the clean-cut type, shows a general inclination to the east of about 28 degrees. When traced southwards the zone becomes more steeply inclined, and in the region of Alp Fjord, a distance of 80 miles from Junction Valley, the thrust-system has passed into a reversed fault. The tilting up of the thrust-system suggests the presence of a buttress in the south; the rocks are cut into slices by small horizontal thrusts at Cape Alfred, and this locality is situated along the supposed northern margin of the buttress. The age of the movements is Caledonian. It is thought that the threefold repetition of Franz Josef Beds and Metamorphic Complex is due to the westward advance of thrust-wedges, and that the belts of Metamorphic Complex represent remnants derived from the rising floor of the East Greenland geosyncline on its extreme western margin.

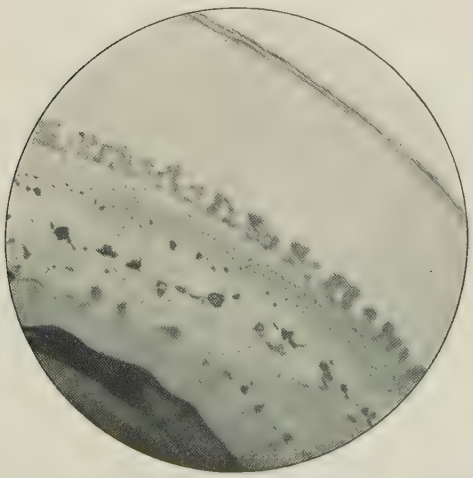
[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

Fig. 1



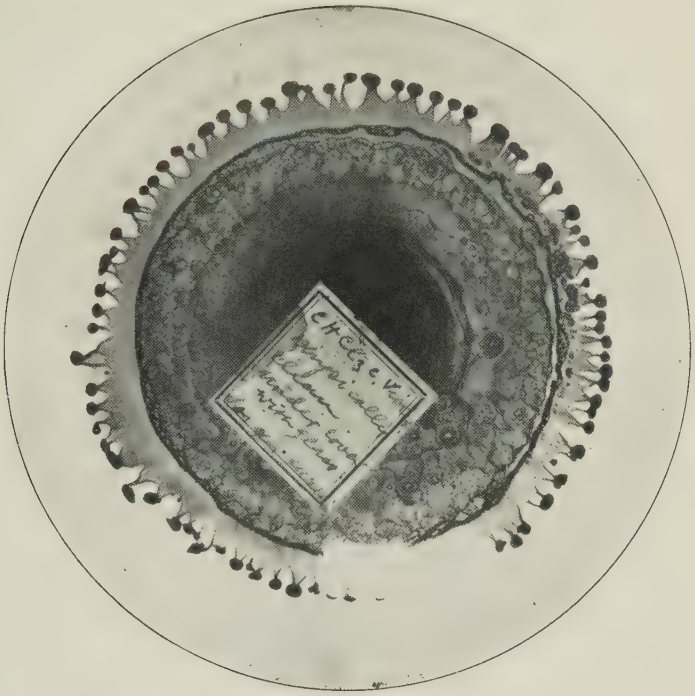
Saturated solution of Anilin-Violet in chloroform under cover over water to retard evaporation. × 3. Duration of reaction, 20 min.

Fig. 2.



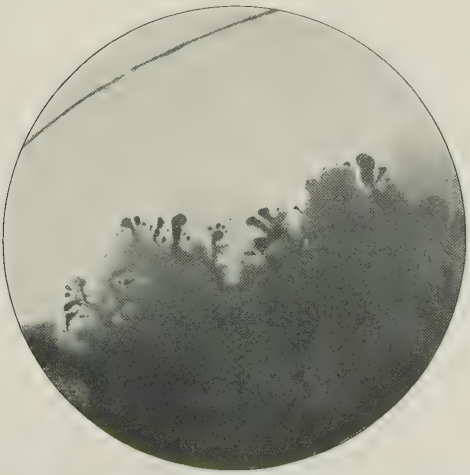
Acetone c. Anilin Violet. × 3. Fenestrated appearance.

Fig. 3.

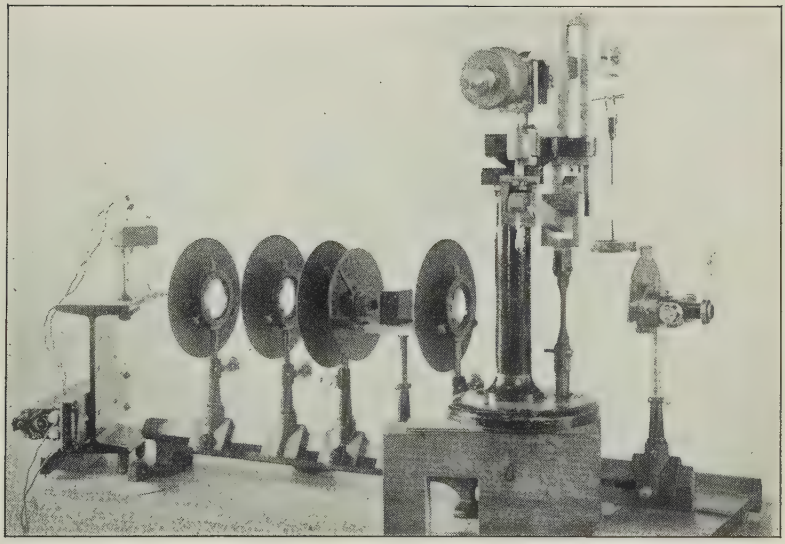


Chloroform c. Anilin-Violet under cover, as in fig. 1. Nat. size.
8 hours' reaction.

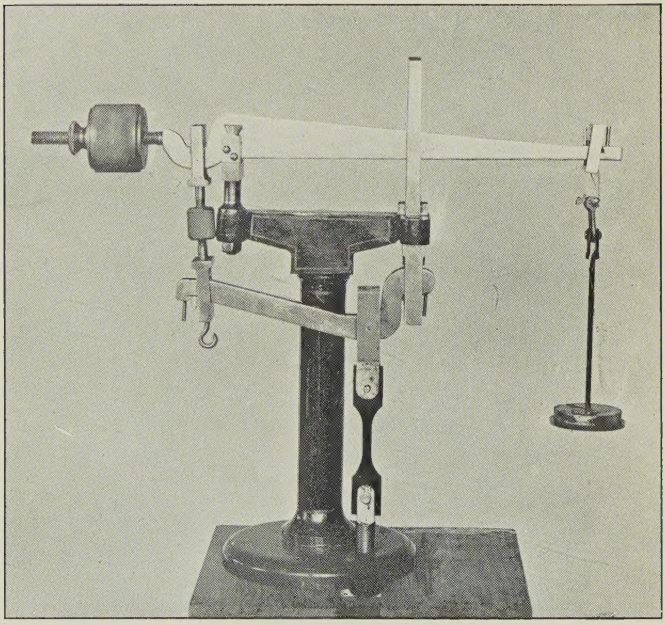
Fig. 4.



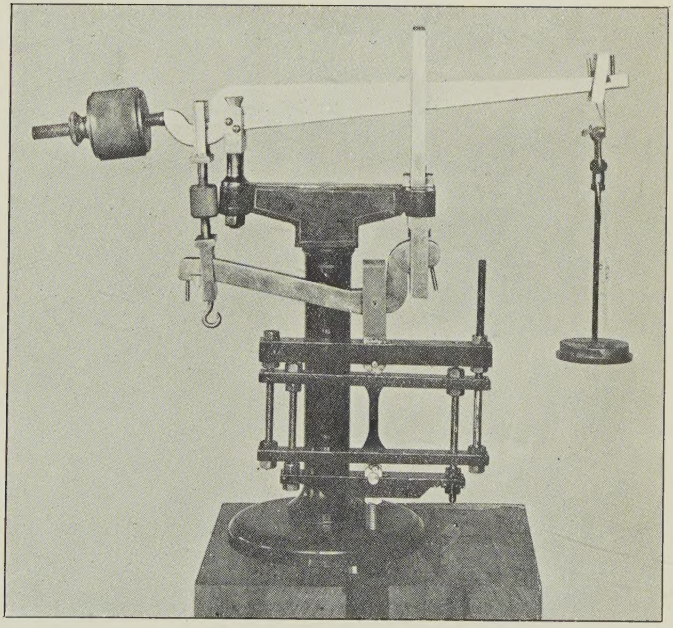
Alcohol and Sulphuric Ether, equal parts, c. Anilin Violet. × 3
Note secondary droplets.



General arrangement of the apparatus used.



Tension device.



Compression device.